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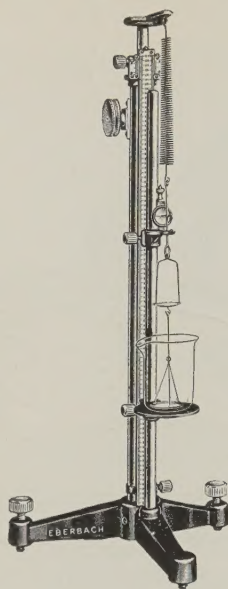
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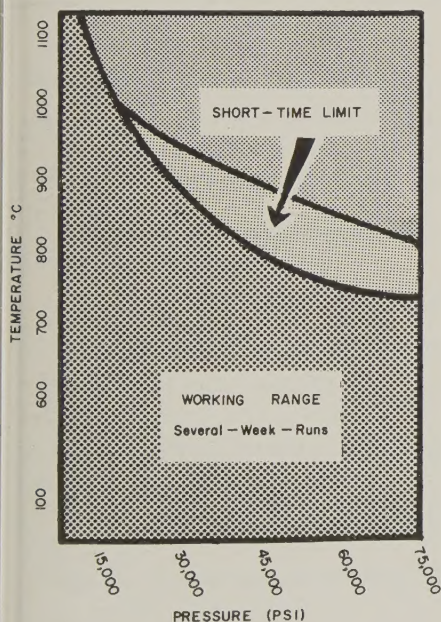
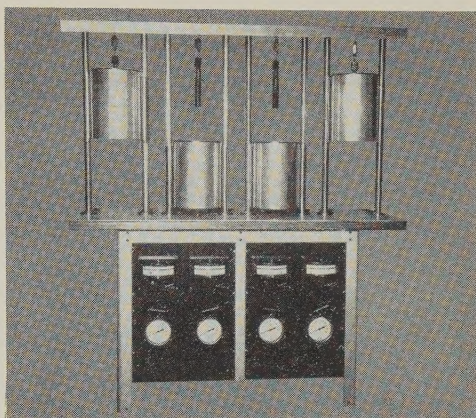
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THE AMERICAN MINERALOGIST

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Nos. 9 and 10

GOWERITE, A NEW HYDROUS CALCIUM BORATE, FROM THE DEATH VALLEY REGION, CALIFORNIA*

RICHARD C. ERD, JAMES F. McALLISTER AND HY ALMOND,†
U. S. Geological Survey, Claremont, California

ABSTRACT

Gowerite is a new hydrous calcium borate, $\text{CaO} \cdot 3\text{B}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$, from the Furnace Creek borate deposits of the Death Valley region, California. Globular minute clusters of gowerite form from the weathering of colemanite and priceite veins in some basaltic rocks in the Furnace Creek formation of late Tertiary age. Associated with gowerite are ulexite, meyerhofferite, ginarite, sassolite, hydroboracite, and an undescribed magnesium borate.

Gowerite is monoclinic and is optically biaxial (+), $\alpha = 1.484 \pm 0.002$, $\beta = 1.501 \pm 0.002$, $\gamma = 1.550 \pm 0.002$, $2V = 63^\circ$ (calc.), $r > v$ slight, $Y = b$, $Z \wedge c = 27^\circ$. Hardness 3, specific gravity 2.00 ± 0.01 .

Two chemical analyses of the mineral gave: CaO, 15.54, 15.46; SrO, 0.71, 0.71; B_2O_3 , 58.14, 58.05; H_2O , 25.75, 25.77; total 100.14, 99.99 per cent.

Synthetic calcium hexaborate pentahydrate is identical with gowerite. The strongest lines of the x-ray powder patterns of both are at 8.2 Å (10), 4.11 Å (5), 3.19 Å (6), and 2.73 Å (5).

The mineral is named in honor of Mr. Harrison P. Gower of the U. S. Borax & Chemical Corporation, Los Angeles, California.

INTRODUCTION

The mineral described in this paper was first noted by McAllister in July 1955 in some samples of efflorescent borates from the Mott open cut in the Furnace Creek area of the Death Valley National Monument, California (Fig. 1). His study of the optical properties of the material indicated that the mineral was distinct from any known borate mineral. This was confirmed by Robert D. Allen‡ who continued the optical study and prepared an x-ray powder pattern. Later Erd refined these data and made the mineralogical studies reported here.

A preliminary qualitative chemical examination by Almond of a very small quantity of the mineral showed it to be a hydrous calcium borate

* Publication authorized by the Director, U. S. Geological Survey.

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‡ Present address, Jet Propulsion Laboratory, California Institute of Technology, Pasadena, California.

with a minor amount of strontium. An adequate amount of material for quantitative analysis was not available, however, until McAllister found a new occurrence of the mineral at the Hard Scramble claim in the Furnace Creek area. The mineral was then found to have the same composition, $\text{CaO} \cdot 3\text{B}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$, as the calcium hexaborate pentahydrate which was synthesized by H. K. Gode in 1949.

This mineral, $\text{CaO} \cdot 3\text{B}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$, is named gowerite in honor of Mr. Harrison P. Gower, of the U. S. Borax & Chemical Corporation, who for many years was in charge of the company's mining operations in Death Valley. Mr. Gower has shown many kindnesses to members of the U. S. Geological Survey's borate project and he conducted them to the principal borate deposits in the Furnace Creek area including the Mott colemanite deposit where gowerite was subsequently discovered.

OCCURRENCE

Gowerite has been found at four localities in the Furnace Creek borate deposits of the Death Valley region, California (Fig. 1). They are on patented mining claims of the Pacific Coast Borax Company and in Death Valley National Monument. The new mineral was first found at the Mott open cut, which is on a colemanite prospect three-fourths of a mile in a straight line S. 17° E. of the upper or eastern junction of the Twenty Mule Team Canyon road with California highway 190. The Mott open cut (loc. 1, Fig. 1) is half a mile up a dry stream channel southeast of the side road. Locality 2, where gowerite is more abundant, is on the Hard Scramble claim about 5 miles southeast of the Mott prospect. The Hard Scramble occurrence is on the western slope of low foothills of the Black Mountains 1.9 miles in a straight line N. 72° W. of Ryan and about 1.2 miles up a wash south of the Dantes View road. The third locality, between the other two, is 1.4 miles S. 43° E. of the Mott open cut and 0.6 mile north of the De Bely mine. Locality 4 is 3,000 feet N. 72° W. of Ryan.

At the gowerite localities colemanite and priceite veins, generally less than 2 inches thick, occur in altered fragmental olivine basalt. The borate-veined basalt is in the Furnace Creek formation (Noble, 1941, p. 955-956) of late Tertiary age and lies stratigraphically above the main zone of colemanite and ulexite, which is in lake and stream sediments near the base of the formation. The gowerite is restricted to a weathered zone where the colemanite and priceite veins waste away within a few feet of the present surface of the hillsides and leave irregular aggregates of alteration products. The alteration products rarely continue to the surface, but as a rule they end under a thin crust of slope debris.

Among these products of weathering at many localities thus far ex-

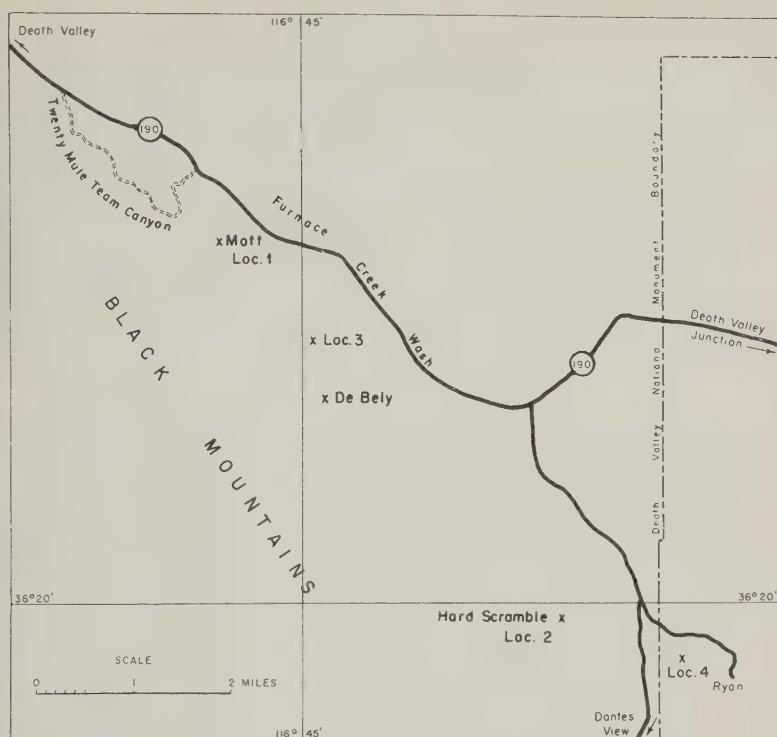


FIG. 1. Index map of a portion of the Death Valley National Monument, showing the localities where gowerite has been found.

amined, gowerite is one of the rarer borates, like sassolite and hydroboracite, in contrast to consistently abundant fluffy ulexite. Others, such as ginorite, meyerhofferite, colemanite, and a magnesium borate of uncertain identity, seem to be intermediate in abundance. Associated minerals commonly include gypsum, thenardite, and some limonite.

In the Mott open cut some of the scarce gowerite is in globular clusters (to ten mm. in diameter) of radiating small blades on remnants of a colemanite vein and is closely associated with crusts and clusters of subhedral crystals of meyerhofferite, some gypsum, and a small quantity of hydroboracite. Some of the gowerite at Mott forms small clusters in the loose aggregate from the weathered basalt, like the much more abundant ginorite associated with sassolite (Allen and Kramer, 1957, p. 56) nearer the surface. Ulexite occurs throughout the weathered zone but is concentrated in the upper part. Ulexite appears to be the only alteration product of colemanite in the calcareous sedimentary rock adjacent to the basaltic rock.

The more abundant gowerite at the Hard Scramble locality is in compact globular clusters, commonly from 1 to 10 mm. in diameter, within loose material weathered from the underlying basaltic rock and on vein-like coherent aggregates of meyerhofferite produced also by the weathering of the same priceite veins. Ulexite, ginorite, and gypsum occur with the gowerite but are more widely distributed in the weathered material above the veins. Unlike those at the Mott locality, the alteration products at the Hard Scramble are derived from priceite, and no sassolite has yet been found among them. The mineralogical observations in this paper were made on material from the Hard Scramble locality. No differences were noted in the properties of gowerite from the other localities.

PHYSICAL PROPERTIES

Gowerite has distinct cleavage parallel to the terminating face (001?) and imperfect cleavage parallel to {100?}. The mineral is brittle and has an uneven fracture. The hardness is 3. Its specific gravity, (D_4^{20}) determined by sink-float in a mixture of bromoform and carbon tetrachloride is 2.00 ± 0.01 . The color of aggregates is white; individual crystals are colorless, transparent, and have a vitreous luster. The streak is white.

Gowerite displays no fluorescence with short or long wave ultraviolet radiation and is not sensibly thermoluminescent.

OPTICAL PROPERTIES

Gowerite is colorless and non-pleochroic in transmitted light. It is biaxial (+) and has the following optical properties:

	n	
α	1.484 ± 0.002	$2V = 63^\circ$ (calc.)
β	1.501 ± 0.002	$r > v$ slight
γ	1.550 ± 0.002	

It has positive elongation. The optic orientation is $Y=b$, $Z \wedge c = 27^\circ$. Viewed on {100?} many of the crystals show an apparent slight inclined extinction. This is probably due to the difficulty of obtaining correctly oriented individuals and to poorly formed crystals.

CRYSTALLOGRAPHY

Morphology

Crystals of gowerite are long prismatic [001] to needlelike and are grouped in radiating globular clusters. The dimensions of an average single crystal are 0.8 mm. in length by 0.06 mm. and 0.02 mm. in width and breadth. The largest crystal observed was 1.5 mm. long.

Prismatic faces are striated parallel to [001]. The terminating form

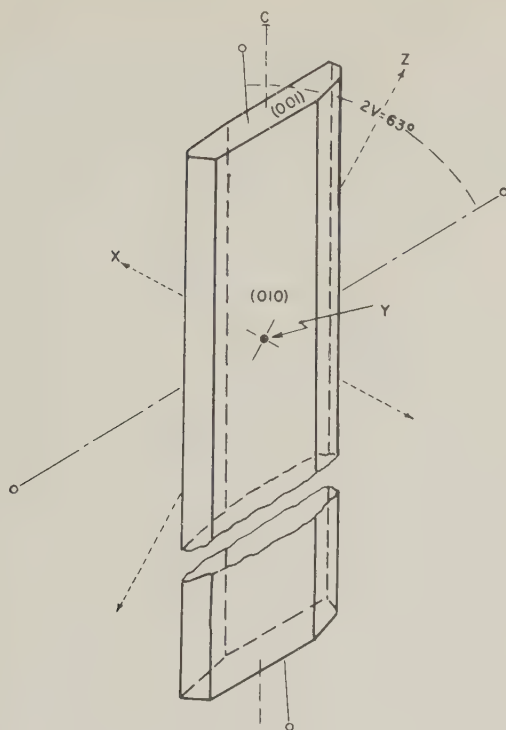


FIG. 2. Optical orientation and approximate habit of gowerite.

$\{001\}$ and the cleavage plane parallel to it make an angle of approximately 60° to $[001]$ in sections parallel to $\{010\}$.

A sketch of a typical gowerite crystal is shown in Fig. 2. This is intended only to give an approximate idea of the habit and optical orientation, and inter-edge and interfacial angles shown should not be taken seriously as to value or as an indication of symmetry. Study of the crystals by x-ray single crystal techniques points to monoclinic symmetry (Joan R. Clark, private communication). Goniometric measurements and x-ray crystallographic and structural data are being obtained by Joan R. Clark and Charles L. Christ.

X-ray powder data

Powder diffraction data for gowerite and synthetic calcium hexaborate pentahydrate, shown in Table 1, were obtained with a Norelco diffractometer over the range $2\theta = 2^\circ - 150^\circ$ using unfiltered iron radiation. Powder photographs using iron radiation with a manganese filter were taken as a check on the diffractometer data.

TABLE 1. X-RAY POWDER DATA FOR GOWERITE AND SYNTHETIC $\text{CaO} \cdot 3\text{B}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$
Unfiltered iron radiation(Only lines due to FeK_α radiation, $\lambda = 1.9373 \text{ \AA}$, are reported)

Gowerite		$\text{CaO} \cdot 3\text{B}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$		Gowerite		$\text{CaO} \cdot 3\text{B}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$	
d_{hkl}	I	d_{hkl}	I	d_{hkl}	I	d_{hkl}	I
9.18	2	9.15	3	2.05		2.05	
8.23	10	8.21	10	2.00		2.01	
6.61	*	6.59	*	1.995		1.995	
5.64		5.63				1.970	
5.52		5.52		1.946		1.943	
5.40	1	5.39	1	1.924		1.924	
5.15	1	5.13	1	1.896		1.897	
4.91	1	4.90	1	1.868		1.868	
4.11	5	4.11	6	1.865			
4.07	2	4.07	3	1.797	1	1.795	1
3.95				1.755		1.755	
3.92	1	3.92	1	1.730	1	1.728	1
3.88	1	3.88	1	1.590	1	1.586	1
3.85	2	3.84	3	1.562		1.561	
3.74		3.74		1.530		1.529	
3.36	1	3.35	2	1.476		1.477	
3.32		3.33		1.465		1.465	
3.23	1	3.23		1.438		1.438	
3.19	6	3.19	5	1.419		1.419	
3.15	2	3.14	3	1.401		1.402	
3.06	1	3.05	1	1.379		1.380	
3.01		3.01		1.369		1.369	
2.97	1	2.96	1	1.357		1.357	
2.96				1.302		1.305	
2.93	1	2.93	1	1.290		1.291	
2.82	1	2.82	2	1.228		1.229	
2.77	1	2.77		1.219		1.220	
2.73	4	2.73	5	1.212		1.212	
2.65	2	2.65	3	1.203		1.203	
2.54	1	2.53	1	1.194		1.194	
2.50				1.178		1.178	
2.46		2.46				1.152	
2.29	1	2.29	2	1.120		1.120	
2.17	1	2.17	1	1.097		1.098	
2.13	1	2.13		1.082		1.082	
2.11		2.11		1.070		1.070	
2.08		2.07		1.062		1.062	
2.06	1	2.06	1	1.050		1.051	

* Blank spaces indicate intensities of less than 1.

The intensities of the set of spacings at 8.23, 4.11, 2.73, and 2.06 Å in the diffractometer charts were greatly increased by aligning uncrushed fibers of gowerite on a glass slide either parallel to or perpendicular to the incident x -ray beam. This preferred orientation was minimized by grinding to -400 mesh. For the same reason the sphere mount technique of Hildebrand (1953) was employed in obtaining the powder photographs.

CHEMICAL PROPERTIES

Analysis

Two samples of the purified mineral from the Hard Scramble locality were carefully prepared by different persons. Of these a 0.1 g. sample and a 0.2 g. sample respectively were used for the borate, calcium, and strontium determinations. Separate fractions of the original material were used for the water determination. The mineral was dissolved in dilute hydrochloric acid and diluted to 100 ml. Aliquots were taken for calcium and borate determinations. Borate was determined by titration with standard sodium hydroxide after addition of mannite to the neutralized borate solution (Scott, 1939). Calcium was determined by titration with the disodium salt of ethylenediaminetetraacetic acid, commonly known as EDTA, as outlined by Shapiro and Brannock (1956). A standard series of solutions containing the analyzed amounts of calcium and borate were prepared with different amounts of strontium. The amount of strontium in gowerite was determined, using a Beckman D. U. flame photometer and photomultiplier attachment, by bracketing the unknown strontium between two known values and then interpolating. Inasmuch as strontium reacts with EDTA, a correction was made for the calcium determination to compensate for the EDTA used by the strontium.

Water was determined by heating a weighed sample to 550° C. in a thermostatically controlled electric furnace, then determining loss of weight of the sample. It was found that at high temperatures 700° C. — large losses of B_2O_3 resulted from heating.

The analytic results are given in Table 2 in which the formula of gowerite is shown to be $CaO \cdot 3B_2O_3 \cdot 5H_2O$ (or $CaB_6O_{10} \cdot 5H_2O$).

Synthesis

Calcium hexaborate pentahydrate, $CaO \cdot 3B_2O_3 \cdot 5H_2O$, was first synthesized by H. K. Gode (1949). His paper was not available to us but, by a slight modification of his synthesis as described in *Chemical Abstracts*, Erd was able to prepare a compound which has an x -ray powder pattern nearly identical with that of gowerite (Table 1). This synthetic gowerite was obtained from a mixture of 20 g $Ca(C_2H_3O_2) \cdot H_2O$ and 40 g H_3BO_3 in

100 ml. of water that was held at a temperature of 35° C. and stirred continuously for 24 hours. The pH of the solution at the beginning and end of the reaction was approximately 5. The product was an extremely fine-grained precipitate of nearly pure synthetic gowerite. Larger crystals, with the same habit and radiating structure of natural gowerite, were grown at room temperature in a mixture of the same composition in a period of 18 days (without stirring).

The density of 2.12 reported by Gode for his synthetic material agrees reasonably well with the value of 2.00 which we obtained for natural and synthetic gowerite.

Solubility data

Gowerite is soluble with difficulty in cold water; moderately soluble in hot water. Gode (1949) obtained a figure of 6.03 g/liter at 20° C. for the synthetic material. Gowerite is readily soluble in cold dilute acids and alkalis and is slowly dissolved by cold 30 per cent hydrogen peroxide. It reacts with sulfuric acid to give gypsum and sassolite. The mineral is apparently insoluble, or only slightly soluble, in methyl alcohol.

Differential thermal analysis

Differential thermal analysis curves of natural and synthetic gowerite (prepared by Erd) were obtained with a portable unit following the procedure described by Allen (1957). Both curves show three endothermic reactions whose initial and trough temperatures are:

	Initial temperature (° C)	Trough temperature (° C)
Gowerite	150	190
	210	270
	440	460
CaO·3B ₂ O ₃ ·5H ₂ O (Synthetic)	140	170
	210	250
	440	460

These reactions represent loss of water and agree fairly well with Gode's thermal analysis of the synthetic material. He found that his synthetically prepared CaO·3B₂O₃·5H₂O loses the first mole of water at 85°, the second between 85° and 110°, the third and fourth at 230°, and the last at 480° C. A glass ($\eta=1.558$) is formed when gowerite is heated to about 500° C. and the runs were stopped at 550° C. to prevent fusion in the sample block.

TABLE 2. CHEMICAL ANALYSES OF GOWERITE

	Weight per cent*			Ratios	Calculated composition for $\text{CaO} \cdot 3\text{B}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$
	Sample 1	Sample 2	Average		
CaO	15.54	15.46	15.50	1.00 or 1 (1×1.00)	15.79
SrO	0.71	0.71	0.71		
B_2O_3	58.14	58.05	58.10	2.95 or 3 (3×0.98)	58.84
H_2O	25.75	25.77	25.76	5.05 or 5 (5×1.01)	25.37
	100.14	99.99	100.07		100.00

* Hy Almond, U. S. Geological Survey, *Analyst*, 1957.

Pyrognostics

Upon heating in a closed tube, gowerite decrepitates, loses water, and turns white and translucent to opaque. Before the blowpipe, gowerite decrepitates, then fuses to an opaque enamel bead.

Although gowerite becomes a glass at a temperature of 500° – 550° C., the sharp outlines of the crystals are preserved. The glass begins to soften at about 600° C. and is completely melted by 660° C. to yield two immiscible liquids. With prolonged heating, during which B_2O_3 is driven off, only a clear liquid remains from which $\text{CaO} \cdot \text{B}_2\text{O}_3$ crystallizes in transparent prismatic crystals. The melting point of 900° reported for the synthetic material by Gode seems unaccountably high.

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AN X-RAY STUDY OF UMOHOITE*

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ABSTRACT

Precession photographs of umohoite from Marysville, Utah, indicate a primitive orthorhombic unit cell with dimensions $a_0=6.32$ Å: $b_0=7.48$ Å: $c_0=12.4$ and $14.5-17.0$ Å. The range of c_0 with humidity and with temperature is established. X-ray powder data for umohoite with $c_0=12.4$ Å are listed, and indices have been assigned on the basis of the cell dimensions given. Powder data are also furnished for material with $c_0=14.5$ Å.

INTRODUCTION

A new occurrence of the hydrous uranyl molybdate, umohoite, has recently been described (Coleman and Appleman, 1957). In addition, work is now in progress in the mineralogical laboratory at Columbia University by Miss P. K. Hamilton on hydrous uranium-molybdenum minerals which includes another occurrence of umohoite. This has led the author to re-examine, by means of x-rays, some properties of the original umohoite as described by Brophy and Kerr (1953), and Kerr, et al. (1957).

The author wishes to express his gratitude to Professor Paul F. Kerr for initiating this study, supplying the mineral specimens examined, and critically reading the manuscript. Miss P. K. Hamilton and Dr. William A. Bassett have kindly offered suggestions during the course of the work.

SINGLE CRYSTAL DATA

A small rectangular plate of umohoite approximately $.12 \times .09 \times .005$ mm. was cut under the microscope from a larger specimen. A precession photograph of the [001] zone gave sharp reflections using $\text{MoK}\alpha$ radiation. Figure 1 is a precession photograph of this zone taken with $\text{CuK}\alpha$, which is a more reproducible photograph, and demonstrates the pseudo-hexagonal character of the reflections. Because of the excessively long (75 hours) exposures required by molybdenum radiation, $\text{MoK}\alpha$ was only employed for the zero level of the [001] zone. $\text{CuK}\alpha$ was utilized for upper levels of this zone and for the [010] zone.

Initial photographs of the [010] zone involved two sets of reflections corresponding to two values of c_0 , 12.4 and 14.5 Å. Both sets showed diffuse streaking parallel to the c -axis. The $hk0$ reflections were independent of the value of c_0 . At the time the photographs were taken it was found that the 12.4 Å spacing could be maintained throughout the umohoite by circulating warm air (40°C.) about the specimen during the time inter-

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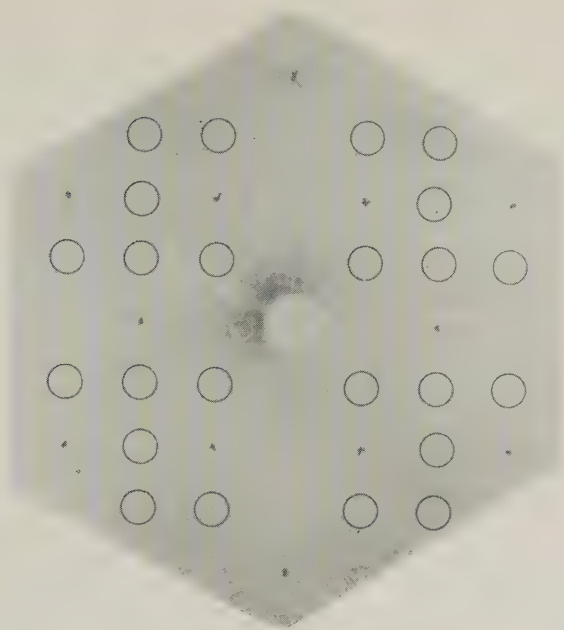


FIG. 1. Umohoite: zero level, c -axis precession photograph, b^* vertical, a^* horizontal; $\text{CuK}\alpha$, 4 hours. Weak reflections are circled.

val of the exposure. All single crystal data given refer to the crystal at this spacing.

The reflections observed indicate the Laue symmetry group nmm . There is no evidence that the orthorhombic symmetry is altered by the increase of c_0 from 12.4 to 14.5 Å. Systematic absences observed are $Ok\ell$ with k odd. The space group is probably one of the following: $Pb2_1m(C_{2v}^2)$, $Pbm2(C_{2v}^4)$ or $Pbmm(D_{2h}^5)$.

Unit cell dimensions obtained from single crystal films and diffractometer runs of powdered material give

$$\begin{aligned} a_0 &= 6.32 \pm .03 \text{ Å.} \\ b_0 &= 7.48 \pm .03 \text{ Å.} \\ c_0 &= 12.4, 14.5 \pm .1 \text{ Å (single crystal).} \\ &14.5\text{--}17.0 \pm .1 \text{ Å (diffractometer).} \end{aligned}$$

Study of the powdered material reveals a continuous variation of c_0 between 14.5 and 17.0 Å, depending upon humidity conditions. The variable c -dimension was noted in the original description of umohoite and considered a function of water content. However, a dimension as small as 12.4 Å has not previously been reported in a specimen at room temperature.

POWDER DATA

Umohoite is fragile and crystals are apt to be destroyed by ordinary grinding. A small quantity of material was effectively powdered by placing it in an electric blender, adding about 100 cc. of distilled water, and allowing the machine to operate at top speed for a few minutes. Diffractometer runs of material oriented for 00 l reflections were made on successive days and the temperature and humidity of the laboratory were measured by means of a sling psychrometer. At temperatures of about 30° C. and a relative humidity above 31 per cent, the 001 reflection was ob-

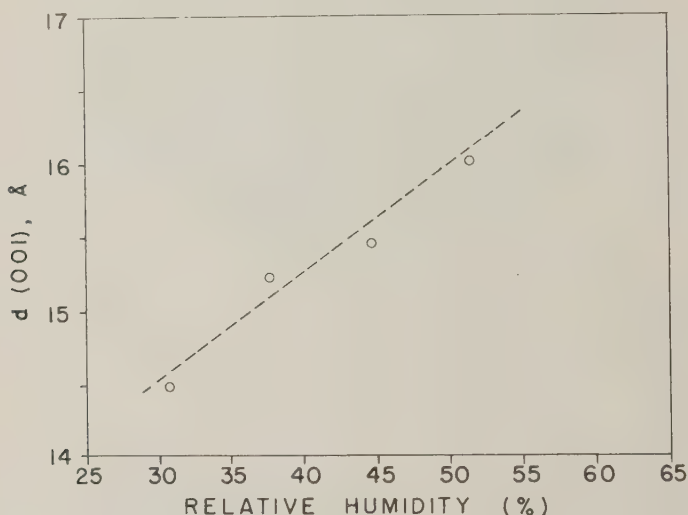


FIG. 2. Variation of (001) with relative humidity.

served to be poorly formed and to vary regularly with small variations in relative humidity (Fig. 2). Dry air circulated about the specimen caused the spacing to drop to 14.5 Å, with relatively well-defined peaks. Moist air circulated in a similar manner caused the spacing to reach 17.0 Å with equally well-formed peaks.

The existence of a 12.4 Å spacing in the case of the single crystal photographs is possibly caused by the combined effects of the more intense beam at the spot focus of the x-ray tube and the adsorptive effect of some clay samples stored in the room containing the single crystal x-ray apparatus.

Some powdered umohoite was deposited on the Pt-Rh sample holder of the high temperature diffractometer (Bassett and Lapham, 1957) and the 001 reflection observed in the course of heating the material to 425° C.

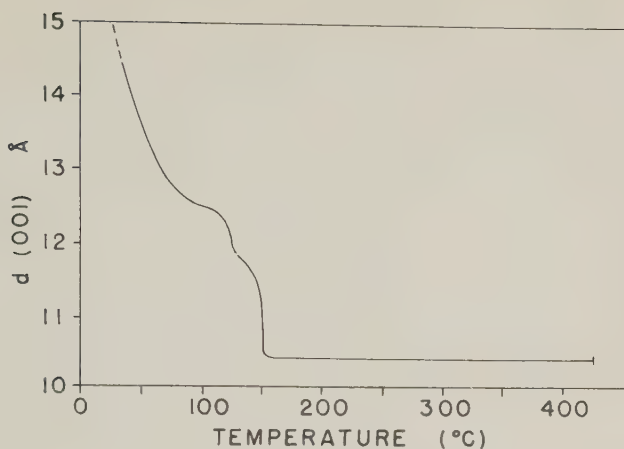


FIG. 3. Variation of (001) with temperature.

(Fig. 3). At 425° C. an unidentified yellow compound was formed. A second specimen was prepared in a similar manner and heated to 350° C. with the result that the 001 reflection yielded a value of 10.6 Å. The material changed in color from the normal pale green of powdered umohoite to a bluish-black. Exposure to steam for several days restored the original pale green color and brought the spacing up to 12.7 Å. No further changes were observed.

A diffractometer run was made of randomly oriented powder under conditions of low humidity which yielded $c_0 = 14.5$ Å. Observed line spacings and intensities are listed in Table 1. Table 2 lists diffractometer data obtained from an unoriented powder which had been kept over-

TABLE 1. DIFFRACTOMETER DATA FOR UMOHOITE ($c_0 = 14.5$ Å).
Cu RADIATION, Ni FILTER

d (Å)	I	d (Å)	I
14.3	1	2.38	1
7.21	10	2.07	2
4.82	4	2.03	2
3.63	2	1.92	1
3.20	5	1.87	1
3.15	4	1.84	1
3.06	4	1.81	1
3.02	3	1.78	1
2.90	4	1.61	2
2.53	1	1.59	1

TABLE 2. DIFFRACTOMETER DATA FOR UMOHOITE ($c_0=12.4$ Å).
Cu RADIATION, Ni FILTER

hkl	d_{calc} (Å)	d_{obs} (Å)	I	d_{obs} (Å)	I
001	12.4	12.2	3	1.95	1
002	6.20	6.18	3	1.87	2
102	4.42	4.40	1	1.83	1
003	4.13	4.13	10	1.79	1
021	3.58	3.57	1	1.78	1
120	3.22	3.20	5	1.75	1
200	3.16	3.15	4	1.73	1
121	3.12			1.71	1
		3.11	2		
004	3.10			1.61	1
201	3.07	3.06	1	1.55	1
122	2.86	2.85	1	1.50	1
023	2.78	2.76	1		
123	2.53	2.54	2		
203	2.51	2.50	1		
220	2.42				
024	2.39	2.40	1		
124	2.23				
204	2.21	2.22	1		
115	2.21				
132	2.17				
214	2.12	2.14	1		
301	2.08				
223	2.08				
006	2.07				
025	2.07	2.07	3		

night in an oven at 50° C. It was found to have a c -dimension of 12.4 Å and has been assigned indices on the basis of the orthorhombic cell determined from single crystal photographs.

IDENTIFICATION OF UMOHOITE

A Patterson projection on (001) indicated an approximately hexagonal arrangement of uranium atoms. The lack of coincidence of the 120 and 200 reflections indicates the deviation of the uranium atoms from a truly hexagonal arrangement. These reflections are strong because of in-phasal scattering of uranium atoms. The fact that they are independent of the value of c_0 makes them especially useful in the identification of umohoite in unoriented specimens, particularly since these reflections persist even through the usual grinding procedures. If specimens are oriented, consideration of the diffractometer curves reproduced by Kerr, et al. (1957) will be most useful if it is understood that these represent the approximate limits of the range of c_0 under normal conditions.

SUMMARY

Unit cell dimensions and powder diffraction data have been obtained for umohoite from the type locality. Umohoite is observed to have a c -dimension which varies directly with normal variations in atmospheric humidity, and inversely with increasing temperature. Ordinarily, c_0 may be expected to lie somewhere between 14.5 and 17.0 Å.

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STUDIES IN THE SYSTEM IRON OXIDE-TITANIUM OXIDE*

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ABSTRACT

Phase equilibria in the system iron oxide-TiO₂ in air have been investigated at temperatures extending from the liquidus to slightly below the solidus. Stability relations among the phases spinel solid solution (FeO · Fe₂O₃ · 2FeO · TiO₂), hematite solid solution (Fe₂O₃ · FeO · TiO₂), pseudobrookite solid solution (Fe₂O₃ · TiO₂ · FeO · 2TiO₂), rutile solid solution, liquid and gas are illustrated in an *apparently* binary diagram obtained by projecting ternary phase relations in the system FeO-Fe₂O₃-TiO₂ into the the join FeO · Fe₂O₃-TiO₂.

INTRODUCTION

Titanium is relatively abundant in the earth's crust; igneous rocks contain an average of approximately 0.64 wt. % of this element. The most important titanium minerals are ilmenite (FeO · TiO₂), titaniferous magnetite (FeO · Fe₂O₃ · 2FeO · TiO₂), rutile (TiO₂) and sphene (CaO · TiO₂ · SiO₂). A great deal of interest has been shown in these lately, especially in ilmenite and the titaniferous magnetites, because of their relation to rock magnetism and their possible use in petrogenesis and geothermometry. These minerals will be important indicators of the environment at time of their formation as the very complicated phase relations in the system FeO-Fe₂O₃-TiO₂ become better understood. Studies of this system will be most useful when completed for an extensive range of both temperature and O₂ partial pressure. In the present investigation a start on the broad study has been made by examining equilibrium relations in a region of relatively high temperature and O₂ partial pressure.

In previous papers emanating from this laboratory (Muan, 1955, 1958; Muan and Osborn, 1956) the special difficulties involved in studying high temperature phase equilibria in iron oxide containing systems have been pointed out. In all systems we have studied and described previously, iron was the only element present whose oxidation state was variable, while the others were noble gas type elements with constant oxidation state such as Si⁴⁺, Al³⁺ and Mg⁹⁺. In the case of the iron oxide-TiO₂ system, additional complications may arise because Ti also exists in different states of oxidation, viz. Ti⁴⁺, Ti³⁺, Ti²⁺, and Ti⁰. When attempting to study this system experimentally one should therefore keep the possibility in mind that Ti as well as Fe may undergo changes in oxidation states unless proper precautions are taken.

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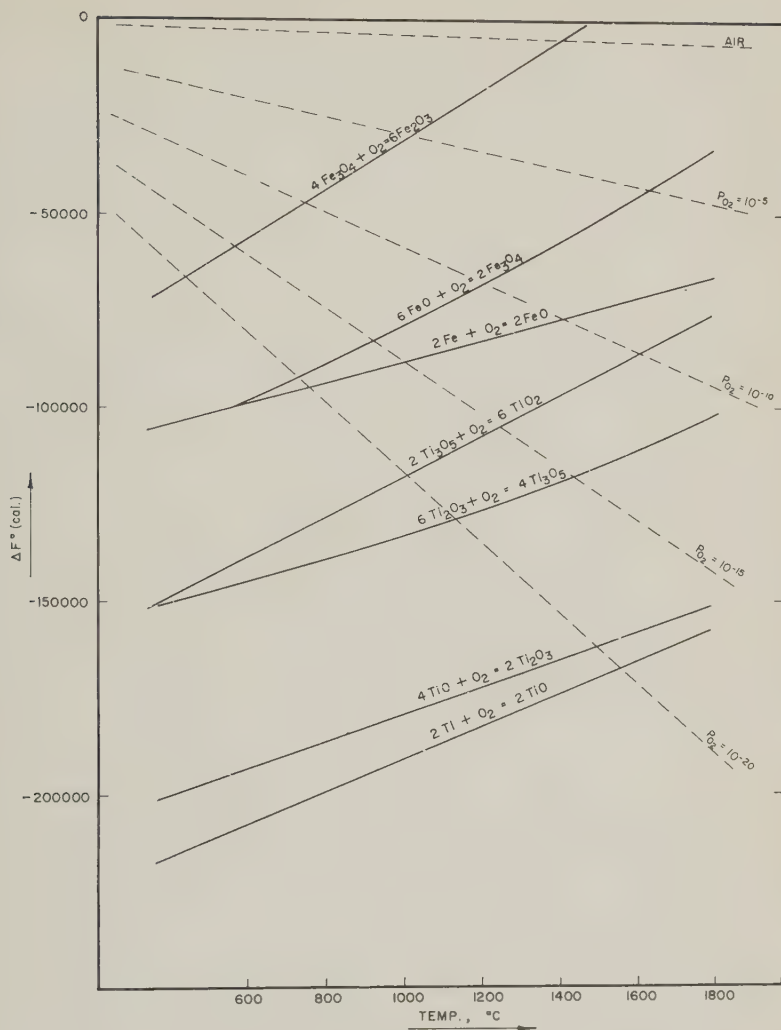


FIG. 1. Diagram showing standard free energy of formation of oxides of Fe and Ti as a function of temperature (solid lines). The curves have been constructed from thermodynamic data tabulated by Coughlin (1954). Dash curves indicate various levels of O_2 partial pressures as labeled in the diagram ($0.21, 10^{-5}, 10^{-10}, 10^{-15}, 10^{-20}$ atm.).

In order to evaluate the relative stabilities of the various oxidation states of Ti and Fe it is instructive to examine a diagram showing standard free energies of formation of the various oxides of these elements as a function of temperature. Such a diagram is shown in Fig. 1, which has been constructed on the basis of data tabulated by Coughlin (1954). The

crystalline phases represented in the case of iron are Fe_2O_3 (hematite), $\text{FeO} \cdot \text{Fe}_2\text{O}_3$ (magnetite), "FeO" (wüstite) and Fe (metallic iron), while the crystalline phases encountered in the case of titanium are TiO_2 (rutile), Ti_3O_5 , Ti_2O_3 , TiO and Ti (metallic titanium). The ΔF° values for these reactions as labeled on the curves in the diagram all refer to 1 mol of oxygen. Hence the ΔF° values are related to the partial pressure of O_2 of the gas phase in equilibrium with condensed phases through the simple relation $\Delta F^\circ = -RT \ln K = RT \ln p_{\text{O}_2}$. Curves representing constant O_2 pressures of 0.21 (air), 10^{-5} , 10^{10} , 10^{-15} and 10^{-20} atm. are plotted as dash lines in Fig. 1. It is evident that the oxides of titanium are much more stable than those of iron. In the case of the pure substances, the lowest oxide of iron, "FeO," can be reduced to metallic iron at O_2 pressures which are still high enough to prevent the structure of the highest oxide of titanium, TiO_2 from decomposing to the structure of the next lower oxide, Ti_3O_5 . In a liquid phase the restrictions on the valence states of the ions imposed by structural requirements are not critical, and continuous variations in the ratios of ions of different valences are possible. Hence the solid lines in the diagram of Fig. 1, pertaining to heterogeneous equilibria, would not be present in the case of a homogeneous liquid phase. The composition of the liquid, expressed in terms of $\text{Fe}^{3+}/\text{Fe}^{2+}$ and $\text{Ti}^{4+}/\text{Ti}^{2+}$ ratios, would vary continuously as a function of temperature and O_2 partial pressure. Because of the much greater stability of the higher valence states of titanium than of iron, ΔF° for the reaction.



would be strongly negative. From the relationship $\Delta F^\circ = -RT \ln K$, it is seen that K would be numerically very large and hence $\text{Ti}^{4+}/\text{Ti}^{2+}$ very much higher than $\text{Fe}^{3+}/\text{Fe}^{2+}$. It is therefore to be expected that in a liquid made up from the oxides of titanium and iron the titanium will remain essentially as Ti^{4+} unless the $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratio is very low. Hence, only if extremely reducing conditions are imposed on the system in an attempt to obtain essentially all iron in the ferrous state is there seemingly any danger of reducing titanium to any appreciable extent to lower oxidation states than Ti^{4+} .

With the above considerations in mind we have chosen to start our study of iron oxide-titanium oxide equilibria by investigating the system in air ($p_{\text{O}_2} = 0.21$ atm.). In choosing to work at a constant O_2 pressure of this level we are studying a section through the system $\text{Fe}-\text{Fe}_2\text{O}_3-\text{TiO}_2$, which is part of the ternary system $\text{Fe}-\text{Ti}-\text{O}$. Methods for describing phase equilibria along an O_2 isobaric section through this system are anal-

* Ti^{4+} and Ti^{2+} are *chosen* as extreme valences of titanium in oxide phases. This choice does not rule out the possible existence of intermediate valence states such as Ti^{3+} ; the latter corresponds formally to a mixture of Ti^{4+} and Ti^{2+} in the ratio 1:1.

ogous to those described for a large number of iron silicate systems, notably $\text{FeO} \cdot \text{Fe}_2\text{O}_3 \cdot \text{SiO}_2$ (Muan, 1955). The most convenient presentation of phase relations is obtained by projecting the 0.21 atm. O_2 isobaric section into the join $\text{FeO} \cdot \text{Fe}_2\text{O}_3 \cdot \text{TiO}_2$. The diagram thus obtained has the appearance of a binary system, but the diagram can be used and interpreted correctly only if due consideration is given to its relation to the ternary system.

PREVIOUS WORK

Several phase equilibrium studies in the pure iron oxide and pure titanium oxide systems have been reported in the literature. The most complete discussion of phase relations in the system Fe-O is found in the papers by Darken and Gurry in 1945 and 1946. A diagram summarizing some of their data which are particularly pertinent to our problem has been presented more recently by Muan (1958). The Ti-O system has attracted considerable interest in recent years. Andersson et al. (1957) are making very comprehensive studies of the phases present in this system. The data obtained by that group will serve to refine the approximate diagram for Ti-O inferred by DeVries and Roy (1954) on the basis of scattered data available in the literature.

Some of the general features of the ternary system $\text{FeO} \cdot \text{Fe}_2\text{O}_3 \cdot \text{TiO}_2$ are fairly well established. Three solid solution series are known to exist in the system: the cubic magnetite-ulvospinel ($\text{FeO} \cdot \text{Fe}_2\text{O}_3 \cdot 2\text{FeO} \cdot \text{TiO}_2$), the hexagonal hematite-ilmenite ($\text{Fe}_2\text{O}_3 \cdot \text{FeO} \cdot \text{TiO}_2$), and the orthorhombic pseudobrookite ($\text{Fe}_2\text{O}_3 \cdot \text{TiO}_2 \cdot \text{FeO} \cdot 2\text{TiO}_2$). In the first of these, magnetite-ulvospinel, a continuous solid solution exists at high temperatures, with exsolution taking place below 600°C . (Kawai, Kume, Sasajima, 1954; Vincent and Wright, 1957). The continuity of the hematite-ilmenite solid solutions seems to be in some doubt. Ramdohr (1926, 1950, 1953) reported that hematite and ilmenite form a continuous solid solution series above 600°C ., while Pouillard (1950) found that two solid solution phases existed together in equilibrium at 950°C . These were described as $(\text{Fe}_{1-y}^{2+}\text{Fe}_{2y}^{3+}\text{Ti}_{1-y}^{4+}) \text{O}_3$ with $y = 1/3$ and $(\text{Fe}_{2-2x}^{2+}\text{Fe}_x^{2+}\text{Ti}_x^{4+}) \text{O}_3$ with $x = 1/3$, corresponding to a miscibility gap extending from approximately 33 to 67 mol%. Nicholls (1955) in a recent review states that it is well known from the work of Ramdohr (1926), as well as Posnjak and Barth (1934), that complete solid solubility exists between ilmenite and hematite above 1050°C . The value of 1050°C . apparently is confirmed by the work of Basta (1953) who showed the miscibility gap to be absent at this temperature.

The most recent and most comprehensive work on the pseudobrookite solid solution series is that of Akimoto and Nagata (1957). On the basis of sealed tube runs they reported a complete solid solution series between

$\text{Fe}_2\text{O}_3 \cdot \text{TiO}_2$ and $\text{FeO} \cdot 2\text{TiO}_2$ at 1200°C . Pouillard (1950), however, in his investigation of the system by a similar method could find no pseudobrookite among the phases appearing at 950°C . Ramdohr (1950) reported that pseudobrookite grows at the expense of hematite-ilmenite solid solution at 1100°C ., and Basta (1953) found that pseudobrookite appears as a new phase in magnetite-ilmenite intergrowths above 950°C . On the basis of these reports it seems reasonable to conclude that a lower temperature limit exists for the stability of pseudobrookite.

Another interesting feature of phase relations in the $\text{FeO}-\text{Fe}_2\text{O}_3-\text{TiO}_2$ system is the mutual solubility of ilmenite and magnetite solid solutions, which is thought to give rise to the intergrowths of magnetite-ulvospinel and ilmenite found in certain mineral deposits. The best evidence for the existence of this solid solution is afforded by Chevallier and Gerard (1950) who succeeded in producing a cubic solid solution crystal whose composition can be calculated as containing 37 mol% ilmenite. This is regarded by Nicholls (1955) as a solid solution not between the cubic and rhombohedral phases but between magnetite and metastable $\gamma\text{-FeTiO}_2$.

Reports on studies of phase relations close to the join $\text{Fe}_3\text{O}_4\text{-TiO}_2$ in the system $\text{FeO}-\text{Fe}_2\text{O}_3\text{-TiO}_2$ have appeared sporadically in the literature during the past 20 years. Junker (1936) made exploratory runs in air at liquidus temperatures with mixtures containing from 0 to 60 Wt.% iron oxide. He concluded tentatively that a "eutectic" exists at about 50 wt.% TiO_2 . Ernst (1943) expanded the work, making runs in sealed tubes as well as in air. He identified the primary phase on the iron oxide side of the "eutectic" as pseudobrookite, which he believed to be stable at its melting point (approximately 1500°C .) and which he thought possessed considerable solubility for TiO_2 and limited solubility for FeO . Ernst also found evidence for the existence of a second "eutectic" between ilmenite-hematite solid solutions and pseudobrookite.

EXPERIMENTAL METHOD

General Procedure

The quenching technique was used in this study. Preheated mixtures of iron oxide and titanium oxide were held in platinum containers in air at constant temperature for a period of time sufficient to ensure equilibrium among gas, liquid and crystalline phases. These samples were then quenched rapidly to room temperature and the phases identified by microscopic and x-ray techniques. Compositions of liquids at liquidus temperatures were determined by chemical analysis of quenched samples.

Materials

Starting materials were reagent grade oxides ("Baker Analyzed"). After drying at 400°C for 18 hrs. the oxides were mixed in desired pro-

portions, ground under alcohol and fired to melting in a gas-air combustion furnace. These samples served as starting materials for runs of long duration for determination of subsolidus equilibria in the quench furnace, and occasionally also for quench runs in the liquidus temperature region. In most cases, however, samples from the gas-air furnace were heated in air at temperatures slightly above the expected liquidus temperature prior to determination of liquidus temperatures. This pretreatment of the mixtures ensured a close approach to the equilibrium $\text{Fe}_2\text{O}_3/\text{FeO}$ ratios of the samples and decreased the time necessary for equilibration runs in the quench furnace.

Platinum crucibles saturated with iron were used to contain the mixtures during prefiring in the gas-air furnace, and small envelopes made from thin platinum foil served as containers for samples during the quench runs. The use of platinum as material for containing iron oxide bearing samples does not cause any complications in studies carried out at relatively high levels of O_2 partial pressures, such as that of air ($p_{\text{O}_2} = 0.21$ atm.) used in the present investigation. For a more detailed discussion of this problem the reader is referred to a previous paper from this laboratory (Muan, 1957).

Furnaces and Temperature Control

The quenching experiments were carried out in vertical tube furnaces wound with platinum or platinum 20% rhodium resistance wire. Temperatures were measured before and after each run with a platinum: platinum-10% rhodium thermocouple calibrated at frequent intervals against standards with melting points defined as follows: $\text{CaMgSi}_2\text{O}_6$, 1391.5° ; CaSiO_3 , 1544° C. The temperatures given on this basis are in accordance both with the Geophysical Laboratory scale and with the 1948 International Scale (Corruccini, 1949; Sosman, 1952). Furnace temperatures were controlled by a second thermocouple inserted close to the heating element and connected through compensating lead wires to a Celetray controller.

Examination of Quenched Samples

Microscopic and x-ray methods were used for identification of phases present in the quenched samples. Examination of polished sections in reflected light was found more informative than examination in transmitted light under the petrographic microscope because of the opacity of most phases. The x-ray technique was used for determination of compositions of solid solution crystals, but could not be used as a tool for determination of liquidus temperatures because the liquids were exceedingly fluid and gave rise to formation of dendritic crystals even during the fastest quenching of the samples in mercury.

Divalent iron contents of samples quenched from liquidus temperatures were determined by wet chemical analysis. The samples were crushed in a Plattner mortar to pass a 100 mesh screen, after which 0.1–0.2 g. were heated to boiling in 20 ml. 1:3 H_2SO_4 in a covered platinum crucible. When steam evolved, 5 ml. HF was added and the solution was allowed to boil for 5–10 minutes. The crucible was then plunged into a 600 ml beaker containing 5 vol.-% H_2SO_4 saturated with boric acid, and the solution was titrated with 0.05 N KMnO_4 . No analysis for total iron oxide content was carried out. Previous experience from similar studies in our laboratories (Muan and Gee, 1956; Muan, 1957; Phillips and Muan, 1958) has indicated that the loss of iron by alloying in the thin platinum foil used as containers for the samples during the equilibrium runs is negligible as long as the partial pressure of O_2 of the gas phase is as high as that of air. Furthermore, the platinum crucibles used for pre-melting the starting mixtures in the more reducing atmosphere of the gas-air combustion furnace were saturated with iron under the conditions prevailing in this furnace through repeated previous use.

RESULTS

Results of quenching experiments are summarized in Table I and illustrated graphically in Fig. 2. Two diagrams are used in this figure in order to show the phase relations as clearly as possible. The upper diagram has the appearance of a binary system with $\text{FeO} \cdot \text{Fe}_2\text{O}_3$ and TiO_2 chosen as components. Stability ranges of the various phases as a function of temperature can be read directly off this diagram. However, because the $\text{FeO}/\text{Fe}_2\text{O}_3$ ratios in all phases present are not equal to 1:1 (molar basis) as in $\text{FeO} \cdot \text{Fe}_2\text{O}_3$, true compositions of condensed phases cannot be represented in terms of the two chosen components. The supplementary triangular diagram $\text{FeO}-\text{Fe}_2\text{O}_3-\text{TiO}_2$ in the lower half of the figure is presented in order to show true compositions of condensed phases. Because of the restrictions imposed by structural requirements, the crystalline phase compositions will vary essentially along parts of straight lines in this diagram, corresponding to binary solid solution series. There are three such series in the system $\text{FeO}-\text{Fe}_2\text{O}_3-\text{TiO}_2$, indicated by light straight lines in Fig. 2. One is the magnetite-ulvospinel ($\text{FeO} \cdot \text{Fe}_2\text{O}_3-2\text{FeO} \cdot \text{TiO}_2$) series of solid solution crystals with spinel structure, the second is the series between hematite (Fe_2O_3) and ilmenite ($\text{FeO} \cdot \text{TiO}_2$) with hexagonal α - R_2O_3 structure, and the third is the series with pseudobrookite structure between the composition points $\text{Fe}_2\text{O}_3 \cdot \text{TiO}_2$ and $\text{FeO} \cdot 2\text{TiO}_2$.*

* In order to obtain experimentally compositions throughout these solid solution series, one has to either vary the O_2 partial pressure over wide limits or work with sealed containers.

TABLE I. RESULTS OF QUENCHING EXPERIMENTS

Temp. of Quench- ing Run (C °)	Phases Present*	Temp. of Run for Anal. (C °)	Initial Comp. (Wt. %)		Comp. after Equil. (Wt. %) (by analysis)		
			Fe ₃ O ₄	TiO ₂	FeO	Fe ₂ O ₃	TiO ₂
1555	Magn.(ss)		99	1			
1515	Magn.(ss)						
1477	Magn.(ss)+Hem.(ss)						
1555	Magn.(ss)+Liq.		98	2			
1515	Magn.(ss)+Hem.(ss)						
1477	Magn.(ss)+Hem.(ss)						
1571	Liq.		97	3			
1531	Magn.(ss)+Liq. (tr.)						
1520	Magn.(ss)+Hem.(ss) (tr.)						
1469	Magn.(ss)+Hem.(ss)						
1441	Magn.(ss)+Hem.(ss)						
1420	Hem.(ss)						
1562	Liq.	1,565	95	5	25.5	69.5	5.0
1554	Magn.(ss) (tr.) +Liq.						
1551	Magn.(ss) (tr.) +Liq.						
1547	Magn.(ss) (tr.) +Liq.						
1502	Magn.(ss)+Hem.(ss)						
1547	Liq.		93	7			
1542	Magn.(ss)+Liq.						
1524	Magn.(ss)+Liq.						
1516	Magn.(ss)+Hem.(ss)						
1504	Magn.(ss)+Hem.(ss)						
1468	Magn.(ss) (tr.)+Hem.(ss)						
1463	Hem.(ss)						
1529	Magn.(ss) (tr.) +Liq.		90	10			
1502	Magn.(ss) (tr.) +Hem.(ss)						
1470	Hem.(ss)						
1441	Hem.(ss)						
1529	Liq.	1,530	88	12	23.6	64.4	12.0
1520	Hem.(ss)+Liq. (tr.)						
1502	Hem.(ss)						
1470	Hem.(ss)						
1441	Hem.(ss)						

* Abbreviations used in this and succeeding tables have the following meanings: Liq. = liquid; Magn.(ss) = crystals of magnetite solid solution; Hem.(ss) = crystals of hematite solid solution; P. Brook.(ss) = crystals of pseudobrookite solid solution; Rut.(ss) = crystals of rutile solid solution; tr. = trace.

TABLE I (continued)

Temp. of Quench- ing Run (C °)	Phases Present*	Temp. of Run for Anal. (C °)	Initial Comp. (Wt. %)		Comp. after Equil. (Wt. %) (by analysis)		
			Fe ₃ O ₄	TiO ₂	FeO	Fe ₂ O ₃	TiO ₂
1534	Liq.		85	15			
1527	Liq.						
1520	Hem.(ss) (tr.) +Liq.						
1511	Hem.(ss)+Liq.						
1508	Hem.(ss)						
1470	Hem.(ss)						
1441	Hem.(ss)						
1513	Liq.	1,518	80	20	21.5	58.5	20.0
1511	Hem.(ss) (tr.) +Liq.						
1494	Hem.(ss)+Liq. (tr.)						
1486	Hem.(ss)+P. Brook.(ss)						
1470	Hem.(ss)+P. Brook.(ss)						
1441	Hem.(ss)+P. Brook.(ss)						
1500	Liq.		75	25			
1496	Hem.(ss)+Liq.						
1492	Hem.(ss)+P. Brook.(ss)						
1470	Hem.(ss)+P. Brook.(ss)						
1523	Liq.	1,530	70	30	18.3	51.7	30.0
1520	P. Brook.+Liq.						
1498	P. Brook.+Liq.						
1492	Hem.(ss)+P. Brook.(ss)						
1545	Liq.	1,545	65	35	20.4	44.6	35.0
1531	P. Brook.(ss)+Liq.						
1495	P. Brook.(ss)+Liq. (tr.)						
1492	P. Brook.(ss)+Hem.(ss) (tr.)						
1396	P. Brook.(ss)+Hem.(ss)						
1549	Liq.		62	38			
1534	P. Brook.(ss)+Liq.						
1524	P. Brook.(ss)+Liq.						
1504	P. Brook.(ss)+Liq. (tr.)						
1502	P. Brook.(ss)						
1486	P. Brook.(ss)						
1413	P. Brook.(ss)						
1555	Liq.		57.5	42.5			
1547	P. Brook.(ss)+Liq.						
1542	P. Brook.(ss)+Liq. (tr.)						
1531	P. Brook.(ss)						
1492	P. Brook.(ss)						
1551	Liq.		57.1	42.9			
1547	P. Brook.(ss) (tr.) +Liq.						

TABLE I (continued)

Temp. of Quench- ing Run (C °)	Phases Present*	Temp. of Run for Anal. (C °)	Initial Comp. (Wt. %)		Comp. after Equil (Wt. %) (by analysis)		
			Fe ₃ O ₄	TiO ₂			
					FeO	Fe ₂ O ₃	TiO ₂
1542	P. Brook.(ss)+Liq.						
1537	P. Brook.(ss)+Liq.						
1528	P. Brook.(ss)						
1492	P. Brook.(ss)						
1400	P. Brook.(ss)						
1553	Liq.	1,555	56.0	44.0	21.3	34.7	44.0
1542	P. Brook.(ss)						
1492	P. Brook.(ss)						
1400	P. Brook.(ss)						
1556	Liq.		54.0	46.0			
1546	P. Brook.(ss) (tr.) +Liq.						
1542	P. Brook.(ss)+Liq.						
1534	P. Brook.(ss)+Liq. (tr.)						
1492	P. Brook.(ss)						
1400	P. Brook.(ss)						
1556	Liq.	1,560	53	47	19.7	33.3	47.0
1549	P. Brook.(ss)+Liq.						
1531	P. Brook.(ss)+Liq. (tr.)						
1527	P. Brook.(ss)						
1400	P. Brook.(ss)						
1549	Liq.		50	50			
1543	Liq.						
1534	P. Brook.(ss)+Liq.						
1516	P. Brook.(ss)+Liq.						
1503	P. Brook.(ss)+Rut.(ss)						
1492	P. Brook.(ss)+Rut.(ss)						
1400	P. Brook.(ss)+Rut.(ss)						
1540	P. Brook.(ss) (tr.)+Liq.	1,545	48	52	18.7	29.3	52.0
1518	P. Brook.(ss)+Liq. (tr.)						
1490	P. Brook.(ss)+Rut.(ss)						
1400	P. Brook.(ss)+Rut.(ss)						
1534	Liq.		42	58			
1525	Liq.						
1520	P. Brook.(ss)+Liq.						
1517	P. Brook.(ss)+Rut.(ss)+Liq. (tr.)						
1511	P. Brook.(ss)+Rut.(ss)						
1552	Liq.	1,555	40	60	16.3	23.7	60.0
1542	Liq.						
1534	Rut.(ss) (tr.) +Liq.						
1517	Rut.(ss)+Liq.						

TABLE I (continued)

Temp of Quench- ing Run (C °)	Phases Present*	Temp. of Run for Anal. (C °)	Initial Comp. (Wt. %)		Comp. after Equil. (Wt. %) (by analysis)		
			Fe ₃ O ₄	TiO ₂	FeO	Fe ₂ O ₃	TiO ₂
1510	Rut.(ss)+P. Brook.(ss)						
1552	Rut.(ss) (tr.)+Liq.		39.5	61.5			
1552	Rut.(ss) (tr.) +Liq.		37.0	63.0			
1529	Rut.(ss)+Liq.						
1516	Rut.(ss)+P. Brook.(ss)						
1511	Rut.(ss)+P. Brook.(ss)						
1520	Rut.(ss)+Liq.		20.0	80.0			
1503	Rut.(ss)+P. Brook.(ss)						
1520	Rut.(ss)+Liq.		17.5	82.5			
1503	Rut.(ss)+P. Brook.(ss)						
1520	Rut.(ss)+Liq.		15.0	85.0			
1503	Rut.(ss)+P. Brook.(ss)						
1470	Rut.(ss)+P. Brook.(ss)						
1420	Rut.(ss)+P. Brook.(ss)						
1543	Rut.(ss).+Liq.		13.0	87.0			
1538	Rut.(ss)+Liq. (tr.)						
1510	Rut.(ss)						
1469	Rut.(ss)						
1420	Rut.(ss)+P. Brook.(ss) (tr.)						
1543	Rut.(ss)+Liq. (tr.)		10	90			
1510	Rut.(ss)						
1470	Rut.(ss)						
1420	Rut.(ss)						
1543	Rut.(ss)		7	93			
1509	Rut.(ss)						
1470	Rut.(ss)						
1420	Rut.(ss)						
1543	Rut.(ss)		5	95			
1505	Rut.(ss)						
1473	Rut.(ss)						
1420	Rut.(ss)						
1543	Rut.(ss)		3	97			
1420	Rut.(ss)						
1543	Rut.		0	100			
1500	Rut.						
1420	Rut.						

In contrast to these compositional variations of crystalline phases along essentially straight lines, the composition of the liquid at liquidus temperatures varies along the irregularly shaped dash curve in the lower diagram of Fig. 2. Light solid and dashed lines are conjugation lines connecting points representing approximate compositions of liquid and crystalline phases coexisting in equilibrium. In order to represent compositions in the upper "binary" diagram in terms of the chosen components $\text{FeO} \cdot \text{Fe}_2\text{O}_3$ and TiO_2 , a method must be adopted for projecting true compositions represented by points in the ternary system on to this join. In accordance with previous practice (Muan and Gee, 1956; Muan, 1958, Phillips and Muan, 1958) we have projected all compositions along straight lines originating at the O corner of the triangle representing the Fe-Ti-O system. These straight lines are the "oxygen reaction lines" representing changes in total composition of condensed phases of mixtures as these react with oxygen of the atmosphere. For purposes of illustration consider the spinel phases designated respectively by a'' and f'' in the upper diagram (Fig. 2). Points a'' and f'' can be located on the lower diagram by the intersections of the dash-dot curves with the $\text{FeO} \cdot \text{Fe}_2\text{O}_3$ - TiO_2 join. Proper projection of these points along the appropriate "oxygen reaction lines," which are very nearly parallel to the Fe_2O_3 -FeO side of the composition triangle, allows estimation of the true compositions of the corresponding spinel phases. Point a'' is found to be the composition shown by the open circle at $\text{FeO} \cdot \text{Fe}_2\text{O}_3$, while the point corresponding to f'' lies further along the spinel solid solution join. The composition of the crystalline phases represented at the points g'' , c'' and d'' of the upper diagram can be obtained by analogous methods.

The most notable features of the diagrams are as follows: Liquidus temperatures decrease as the first amounts of TiO_2 are added to iron oxide, from 1594°C . for pure iron oxide (Darken and Gurry, 1946) to 1524°C . in a mixture containing 12 wt.% TiO_2 , with magnetite (ss) as the primary crystalline phase in this composition range. Hematite (ss) is the primary crystalline phase in the composition range 12–27 wt.% TiO_2 , with liquidus temperatures decreasing from 1524 to 1493°C . A liquid of the latter TiO_2 content is in equilibrium with hematite (ss) as well as pseudobrookite (ss) at what appears as a eutectic situation at 1493°C . This is in reality a univariant situation corresponding to the intersection between the 0.21 atm. O_2 isobar and a ternary univariant line in the system FeO - Fe_2O_3 - TiO_2 along which two crystalline phases coexist in equilibrium with a liquid and a gas phase. However, the existing degree of freedom has been "used up" in our choosing the O_2 partial pressure as that of air. As more TiO_2 is added to the mixtures, pseudobrookite is the primary crystalline phase, and liquidus temperatures

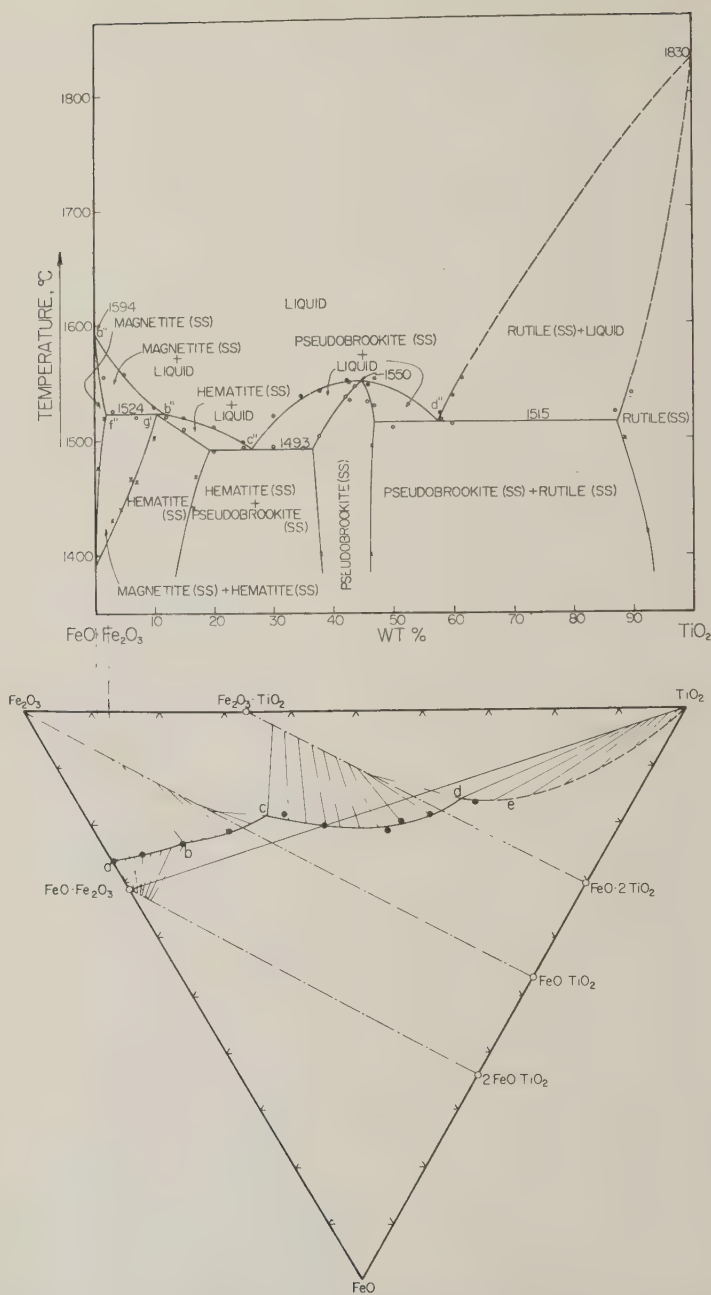


FIG. 2. Diagrams presented in order to show phase relations in the system iron oxide-TiO₂ in air. The upper half of the figure is a diagram with the appearance of a binary

increase. The liquidus curve goes through a maximum at approximately 1550° C. and 45 wt. % TiO_2 , and subsequently decreases to another "eutectic," characterized by the coexistence at 1515° C. of the phases pseudobrookite (ss), rutile (ss), a liquid containing 58 wt. % TiO_2 , and gas of O_2 partial pressure equal to 0.21 atm. With rutile as the primary crystalline phase, liquidus temperatures increase rapidly as the TiO_2 content is increased above 58 wt. %, reaching a maximum of approximately 1830° C. for the pure TiO_2 end member (the latter based on data summarized by DeVries and Roy, 1954).

The most notable feature of the subsolidus phase relations is the marked influence of TiO_2 on the equilibrium decomposition temperature of the sesquioxide ($\alpha\text{-R}_2\text{O}_3$) structure of hematite to the spinel structure of magnetite. This decomposition temperature in air goes up from 1390° C. for the pure iron oxide end member to a maximum of 1524° C. as TiO_2 is added.

A summary of "invariant" situations in the system iron oxide- TiO_2 in air is presented in Table II, and x-ray diffraction data for pseudobrookite and rutile are listed in Table III.

DISCUSSION

One of the most interesting observations made in this investigation is that of the very strong stabilizing influence of TiO_2 on the hexagonal $\alpha\text{-R}_2\text{O}_3$ structure of hematite relative to the spinel structure of magnetite. The addition of as little as 10 wt. % TiO_2 to iron oxide raises the temperature of the hematite to magnetite decomposition from 1390° C. to 1524° C. in air. This observation is important for an understanding of stability relations existing among iron oxide- TiO_2 minerals and may also have some important implications in technology. The change back and forth from one of these structures to the other in response to changes in temperature or O_2 partial pressure or both has been recognized in recent

system, showing the phases present as a function of temperature. Heavy lines are boundary curves. Solid dots, open circles and crosses represent experimentally determined points on liquidus, solidus and subsolidus boundary curves, respectively, based on data contained in Table I. The lower, triangular diagram shows compositions of crystalline and liquid phases. The heavy dash curve *abcde* represents compositions of liquids along the liquidus surface in air. Crystalline phases have compositions approximately represented by parts of the joins $\text{FeO} \cdot \text{Fe}_2\text{O}_3 \cdot 2\text{FeO} \cdot \text{TiO}_2$, $\text{Fe}_2\text{O}_3 \cdot \text{FeO} \cdot \text{TiO}_2$ and $\text{Fe}_2\text{O}_3 \cdot \text{TiO}_2 \cdot \text{FeO} \cdot 2\text{TiO}_2$. Solid circles represent compositions of liquids as determined by chemical analysis. Light solid and dash lines are approximate locations of conjugation lines connecting points representing compositions of liquid and crystalline phases existing together in equilibrium in air. Light dash-dot and dash-double dot lines are auxiliary construction lines as explained in the text.

TABLE II. SUMMARY OF "INVARIANT"* SITUATIONS IN THE SYSTEM
IRON OXIDE-TiO₂ IN AIR

Phases Present	Comp. of Liquid (Wt. %)			Temperature (° C)
	FeO	Fe ₂ O ₃	TiO ₂	
Magn.+Liq.	27	73	0	1,594
Magn.+Hem.	27	73	0	1,390
Magn.(ss)+Hem.(ss)+Liq.	23	65	12	1,524
Hem.(ss)+P. Brook.(ss)+Liq.	18	55	27	1,493
P. Brook.(ss)+Liq.	20	35	45	1,550
P. Brook.(ss)+Rut.(ss)+Liq.	16	26	58	1,515
Rut.+Liq.	0	0	100	1,830

* The phase assemblages listed in reality represent univariant situations in the ternary system Fe-Ti-O. However, the existing degree of freedom has been "used up" in choosing the O₂ partial pressure of the gas phase, and hence the situations may be considered "invariant."

years as an important cause of damage to refractories used in steelmaking furnaces (see for instance a paper by Osborn, 1956). The stabilization of the hematite structure relative to that of magnetite, caused by TiO₂, may be advantageous or disadvantageous as far as refractories behavior

TABLE III. POWDER X-RAY DIFFRACTION DATA FOR PSEUDO-BROOKITE AND RUTILE Fe K_α RADIATION

Pseudobrookite		Rutile	
(57.1 Wt. % Iron Oxide, 42.9 Wt. % TiO ₂)		(TiO ₂)	
<i>d</i> -Spacing	Intensity*	<i>d</i> -Spacing	Intensity*
4.92	W	3.25	S
3.49	S	2.49	W
2.75	S		
2.46	W	2.19	W
2.41	W	1.69	M
2.23	W	1.63	M
2.20	W		
1.97	M		
1.87	M		
1.76	W		
1.67	W		
1.64	W		
1.55	W		

* Abbreviations used have the following meanings: S = strong; M = medium; W = weak.

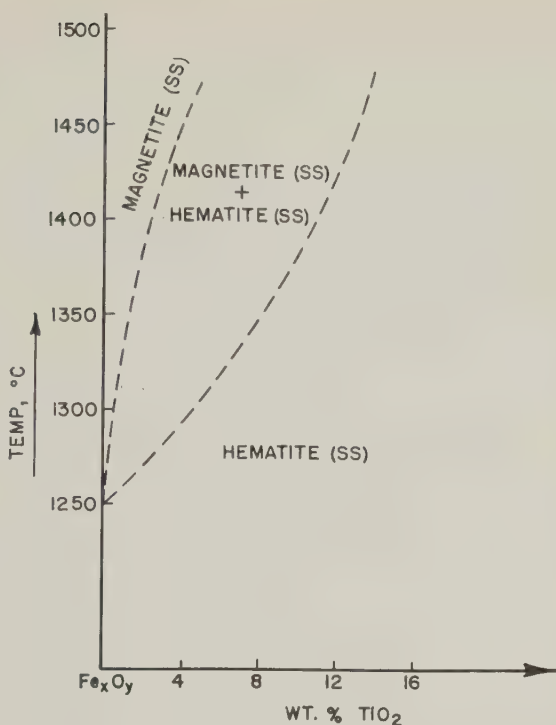


FIG. 3. Sketch presented in order to show approximate stability relations among sesquioxide and spinel phases in system iron oxide-TiO₂ at an O₂ partial pressure of 10⁻² atm.

is concerned, depending on the conditions under which the refractory is being used. Consider for instance first a situation in which an iron oxide-containing refractory body exposed to air is subject to temperature variations in the interval 1300–1500° C. If pure iron oxide is present, a phase change from hematite to magnetite or reverse will tend to make place every time the temperature cycle passes through 1390° C. If on the other hand the iron oxide phase contains 10 wt. % TiO₂, the hexagonal hematite (ss) phase is stable up to 1524° C. in air, and no phase changes will take place in the temperature interval 1300–1500° C. As O₂ partial pressure is reduced, the magnetite (ss) phases will increase its stability range relative to that of hematite (ss). This corresponds to a displacement of the two-phase area spinel (ss)+hematite (ss) in Fig. 2 toward lower temperatures as O₂ partial pressure is decreased. Although quantitative data are not yet available for the system iron oxide-titanium oxide at lower levels of O₂ partial pressures, data for iron oxide permits an estimate of the relations to be expected. The sketch in Fig. 3 illustrates the

situation that may be inferred to prevail where magnetite and hematite coexist at an O_2 partial pressure of approximately 10^{-2} atm. Considering the same temperature range as mentioned above, namely 1300–1500° C., pure iron oxide now remains as the single phase magnetite throughout this range, whereas iron oxide containing 10 wt.% TiO_2 begins to transform from α - Fe_2O_3 to spinel at 1380° C. Hence at this level of O_2 partial pressure (10^{-2} atm.) the presence of TiO_2 may result in damaging phase transformations that did not occur in the presence of pure iron oxide as a constituent of the refractory body.

In contrast to this stabilization by TiO_2 of the hematite phase, which contains essentially all iron as Fe^{3+} , TiO_2 added to liquid iron oxide stabilizes Fe^{2+} relative to Fe^{3+} . This can be seen by an inspection of the lower half of Fig. 2. The heavy dash curve represents compositions of liquids along the liquidus surface, hence temperature is a variable in addition to composition. Because the decomposition of oxide of Fe^{3+} to the oxide of Fe^{2+} is a strongly endothermic reaction, Fe^{3+} is stabilized relative to Fe^{2+} as temperature is decreased, provided O_2 partial pressure and total composition in terms of ratio TiO_2 to total iron oxide remain constant. The stabilizing effect of TiO_2 on Fe^{2+} becomes apparent by following the curve *a b c d e* in Fig. 2 from point *a* on the iron oxide join toward *e* as TiO_2 content increases. The first part of this curve (*a b c*) is pointing approximately toward the TiO_2 corner of the diagram; such a straight line corresponds to constant Fe^{2+}/Fe^{3+} ratios of the liquids. This situation arises because the compositional effect of TiO_2 shifting the equilibrium towards Fe^{2+} , is balanced by an equal effect in the opposite direction of the decrease in liquidus temperature as TiO_2 is added to iron oxide (see upper part of Fig. 2). As the TiO_2 content reaches approximately 27 wt.%, liquidus temperatures start rising rapidly (see upper half of Fig. 2). This causes a discontinuity in the slope of the isobaric curve at *c*, the curve *c-d* bending sharply to the right. The rapid increase in Fe^{2+}/Fe^{3+} ratio of liquids with increasing TiO_2 content at point *c* is the combined result of increasing liquidus temperature and the compositional effect of TiO_2 on the equilibrium. As the TiO_2 content approaches that of the maximum on the liquidus curve (see upper half of Fig. 2), the effect of temperature dies out, and as the liquidus temperatures decrease with further increase in TiO_2 content, the O_2 isobar swings back towards point *d*. Here the TiO_2 content is that of the pseudobrookite-rutile "eutectic," and further increase in TiO_2 content causes a very sharp increase in liquidus temperatures. Hence a discontinuity in the slope of the O_2 isobar occurs at point *d*, the curve bending sharply to the right as TiO_2 content increases beyond this point.

The binary joins between the composition points of the stoichiometric end members have been taken to represent compositions of solid solution

crystals in the three series magnetite-ulvospinel ($\text{FeO} \cdot \text{Fe}_2\text{O}_3$ - $2\text{FeO} \cdot \text{TiO}_2$), hematite-ilmenite (Fe_2O_3 - $\text{FeO} \cdot \text{TiO}_2$) and pseudobrookite ($\text{Fe}_2\text{O}_3 \cdot \text{TiO}_2$ - $\text{FeO} \cdot 2\text{TiO}_2$) in the lower half of Fig. 2. This is an approximation made for the purpose of plotting approximately the conjugation lines giving relations between compositions of crystalline and liquid phases existing together in equilibrium. In the case of the magnetite-ulvospinel solid solution, data are available to indicate that this spinel phase contains less Fe^{2+} than corresponding to the stoichiometric ratio (Darken and Gurry, 1946; Chevallier and Gerard, 1950). Compositions of only two crystalline phases, one from the hematite solid solution and one from the pseudobrookite solid solution field, were determined by chemical analysis in the present investigation. The observed compositions fall reasonably close to the expected joins. In the case of rutile which has dissolved some iron oxide in its structure, the mechanism of substitution is not well known. Work on the system FeO - TiO_2 (to be published) has indicated that both Fe^{2+} and Fe^{3+} ions can be accommodated by the rutile lattice. Therefore, conjugation lines in the region where rutile (ss) is the primary crystalline phase have been drawn to the $\text{FeO} \cdot \text{Fe}_2\text{O}_3$ - TiO_2 join.

SUMMARY

Phase equilibria in the system iron oxide- TiO_2 in air ($p_{\text{O}_2} = 0.21$ atm.) have been studied by the quenching technique.

The relations are represented by a projection into the join $\text{FeO} \cdot \text{Fe}_2\text{O}_3$ - TiO_2 of compositions actually located in the ternary system FeO - Fe_2O_3 - TiO_2 . Points of intersection between the 0.21 atm. O_2 isobar along the liquidus surface and liquidus univariant lines in the ternary system look like eutectic and peritectic points in the apparently binary diagram which results. The main features of the diagram as well as temperatures and phase assemblages at the "invariant" situations are summarized as follows: Hematite is the stable phase of pure iron oxide up to 1390°C . At this temperature hematite and magnetite coexist in equilibrium in air, while magnetite is the stable phase from this temperature up to the liquidus temperature of 1594°C . Magnetite (ss) is the primary crystalline phase in the composition range 0-12 wt. % TiO_2 , with liquidus temperatures decreasing to a minimum of 1524°C . At the latter temperature a "peritectic" situation exists with the following phases present together in equilibrium: Spinel (ss), hematite (ss), liquid, gas ($p_{\text{O}_2} = 0.21$ atm.). Hematite (ss) is the primary crystalline phase in the composition range 12-27 wt. % TiO_2 . At 1493°C . a "eutectic" situation prevails, characterized by the coexistence in equilibrium of hematite (ss), pseudobrookite (ss), liquid and gas ($p_{\text{O}_2} = 0.21$ atm.). Pseudobrookite (ss) is the primary crystalline phase in mixtures between 27 and 58 wt. % TiO_2 , with the liquidus temperature reaching a maximum of 1550°C . at 45 wt. % TiO_2 .

Pseudobrookite (ss), rutile (ss), a liquid containing 58 wt. % TiO_2 and gas exist together in equilibrium at 1515°C . in another "eutectic" situation. Rutile (ss) is the stable phase in mixtures containing more than 58 wt. % TiO_2 , with liquidus temperatures increasing from 1515°C . to the melting point of pure TiO_2 , approximately 1830°C .

The most significant result of the studies made at subsolidus temperatures is the marked stabilization of the hematite structure relative to that of magnetite as TiO_2 is added to iron oxide, the equilibrium temperature in air increasing from 1390°C . for the pure iron oxide end member to a maximum of 1524°C . In the liquid, TiO_2 stabilizes Fe^{2+} relative to Fe^{3+} .

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STABILITY RELATIONS AMONG SOME
MANGANESE MINERALS*

ARNULF MUAN

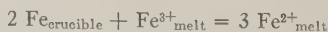
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ABSTRACT

Stability relations among crystalline phases in the system manganese oxide-SiO₂ have been studied in atmospheres of controlled O₂ pressures ranging from 10^{-2.5} to 1 atm. and at temperatures ranging from 973 to 1206° C. The crystalline phases encountered in the present study are Mn₂O₄, braunite (Mn₂O₃(SS)), tephroite (2MnO·SiO₂), rhodonite (MnO·SiO₂(SS)) and tridymite (SiO₂). Equations are given relating O₂ partial pressures and temperatures for 6 different univariant situations characterized by the equilibrium coexistence of gas and three crystalline phases.

INTRODUCTION

Examination of natural minerals as well as laboratory studies of "synthetic minerals" are necessary in order to arrive at intelligent inferences regarding conditions prevailing during formation and alteration of minerals and rocks in nature. Laboratory studies have been concentrated in the past mainly on phase equilibrium investigations in dry silicate systems. Such studies, pioneered by staff members of the Geophysical Laboratory of the Carnegie Institution of Washington and taken up by other groups of geochemists, ceramists and metallurgists, have improved tremendously our understanding of the behavior of liquid and crystalline silicates. Most of these phase equilibrium studies have been restricted to combinations of oxides of noble gas type ions, such as for instance SiO₂, Al₂O₃, MgO, CaO, etc. Notable exceptions are investigations of systems containing iron oxide as a component. Bowen and Schairer (1932) 25 years ago developed an experimental technique for studying such systems, making the runs in iron crucibles in a N₂ atmosphere. The N₂ gas, after purification, contains only very small traces of O₂, but usually enough to cause a very slight oxidation of the crucible. In this way, an O₂ potential in the system is automatically maintained corresponding, at any particular temperature, to the equilibrium between metallic iron and its lowest oxide, "FeO" (wüstite). If the gas is so low in O₂ that the crucible does not oxidize, the O₂ potential of the system is defined by the equilibrium



at any temperature. In both cases the crucible serves to maintain a certain partial pressure of O₂ of the gas phase, and this pressure is low enough

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to keep essentially all iron of the oxide phase(s) in the divalent state. This technique permitted the careful study of phase relations in a large number of important rock forming systems such as for instance "FeO"-SiO₂ (Bowen and Schairer, 1932) and MgO-"FeO"-SiO₂ (Bowen and Schairer, 1935). However, the technique has the shortcoming of not permitting the variation of O₂ pressure independently of temperature. From such studies of "dry" silicate systems at atmospheric pressure, geochemists have branched out during recent years to investigations at high hydrostatic pressures and studies of the influence of water and other volatiles on silicate equilibria, the latter usually in combination with elevated pressures.

Discussions of the problem of the oxygen potential prevailing during the crystallization of magmas have appeared in the literature (Kennedy, 1948), and theoretical derivation of the distribution of elements in a gravitational field has been presented by Brewer (1951). However, very little systematic experimental work has been done on phase relations in mineral systems under controlled, varying O₂ partial pressures. Such studies may well lead to the development of reliable O₂ pressure indicators, or perhaps even a combination of a "geological O₂ barometer" and a geological thermometer.

Studies of iron oxide containing systems under conditions such that the O₂ pressure can be varied as an independent parameter have been carried out by metallurgists for more than 20 years. Particularly important among these studies is the investigation of the system Fe-O by Darken and Gurry (1945, 1946). They used CO₂-CO or CO₂-H₂ gas mixtures to define the O₂ partial pressure, while keeping the total pressure constant at 1 atm. in their experiments. Darken (1948) also studied parts of the system Fe-Si-O and obtained important data regarding subsolidus stability relations among iron oxides and fayalite (2FeO·SiO₂). These studies seem to have received less attention than they deserve among mineralogists and geochemists. The same methods used by Darken and Gurry have been extended to the detailed study of liquidus relations in the system FeO-Fe₂O₃-SiO₂ (Muan, 1955) and the system MgO-FeO-Fe₂O₃-SiO₂ (Muan and Osborn, 1956) in connection with research on steelplant refractories systems. Paths of crystallization under chosen idealized conditions were derived for these systems, and Osborn (in press) has used these principles recently to derive a new theory for the courses of reactions to be expected in the crystallization of a magma under various conditions of O₂ partial pressures.

An experimental study by Flaschen and Osborn (1957) of equilibria in parts of the system Fe-Si-H-O established some general relations between O₂ partial pressure and stability among important dry and hydrated mineral phases in that system. However, because of the experimental diffi-

culties involved, no accurate quantitative figures were obtained that permitted the use of these data as O_2 pressure indicators.

The present paper describes results of a study establishing quantitative relations between O_2 partial pressure and temperature for univariant situations among some manganese oxide containing minerals. It is the first in a series of investigations dealing with systems made up from combination of manganese oxides with other oxides. Silica was chosen as component in addition to manganese oxide in the present study. This work supplements previous investigations of the system manganese oxide- SiO_2 in air (Muan, in press) and under conditions of low O_2 partial pressures (Glasser, 1958). The present investigation was limited to the temperature range from $973^\circ C.$ up to the liquidus, and to O_2 partial pressures in the range $10^{-2.5}$ to 1 atm. The lower temperature limit was dictated by the necessity of working under conditions where reaction rates are high enough for equilibrium to be attained within a reasonable period of time. The range of O_2 partial pressures ($10^{-2.5}$ to 1 atm.) was chosen because all equilibria of particular interest in the present investigation fall in this region for the chosen temperature interval. Whereas working with O_2 pressures above 1 atm. would require experimental techniques entirely different from those used in the present investigation, there would be no particular difficulties working at O_2 partial pressures below the lower limit ($10^{-2.5}$ atm.) used. However, extreme caution must be exercised when working in the range 10^{-3} to 10^{-5} atm. O_2 because of the small "buffering capacity" in that range of the gas mixture generally used. These problems have been discussed in detail in a previous paper (Muan, 1958).

PREVIOUS WORK

Stability relations among the various oxides of manganese have been the subject of numerous studies, but so far no equilibrium diagram for the system Mn-O has been presented. The stability fields of MnO ,* Mn_3O_4 and Mn_2O_3 have been reported in a recent publication by Hahn and Muan (in press); previous data on these equilibria have also been reviewed and discussed in considerable detail in that paper. The diagram in Fig. 1 includes curves for the Mn_2O_3/Mn_3O_4 and Mn_3O_4/MnO equilibria based on their data.

The system manganese oxide-silica in the liquidus temperature region has been studied by a large number of investigators. The most recent work is that carried out by Glasser (1958) who used a CO_2 - H_2 atmosphere to keep essentially all manganese in the divalent state. The reader is re-

* The oxygen to manganese ratio of this phase is known to vary. The simplified formula MnO is used for sake of convenience in this paper.

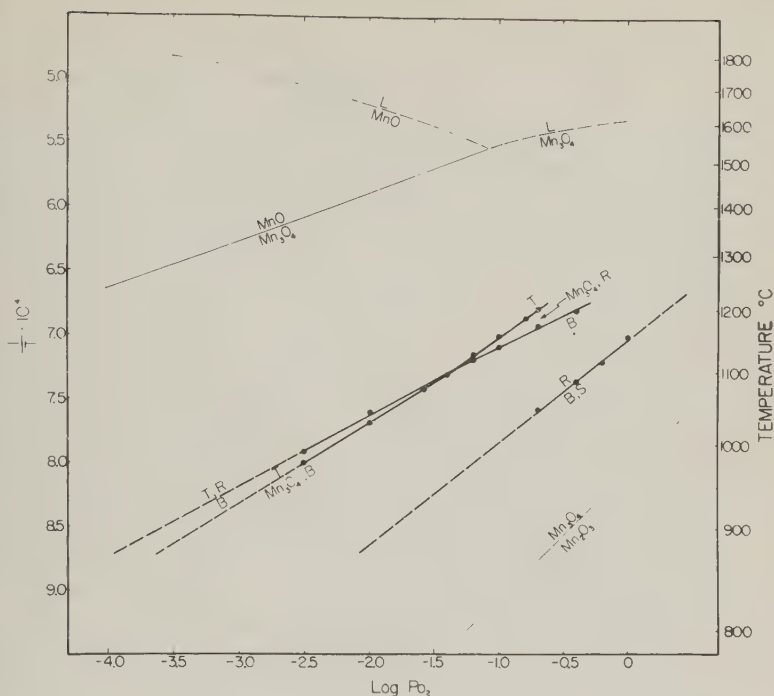


FIG. 1. Diagram illustrating relations of O_2 partial pressure and temperature for univariant equilibria in the system Mn-Si-O. Solid dots represent experimentally determined conditions for equilibrium coexistence of three crystalline phases and a gas, and the solid lines are drawn to pass through these points as closely as possible. Light lines represent conditions for coexistence of a gas and two crystalline phases in univariant equilibrium in the binary system Mn-O, based on data of Hahn and Muan (in press) and of Coughlin (1954). Dashed lines in the diagram are extrapolations into regions where no experimental data are available. Abbreviations used in the diagram have the following meanings: S=silica (tridymite); B=braunite ($Mn_2O_3(SS)$); R=rhodonite ($MnO \cdot SiO_2(SS)$); T=tephroite ($2MnO \cdot SiO_2$); L=liquid.

ferred to his paper also for a review of previous investigations of the system $MnO-SiO_2$. Phase relations in the system manganese oxide- SiO_2 in air in the liquidus region and at subsolidus temperatures were studied recently by Muan (in press). Most remarkable among the relations established in the latter study was the stable existence, in air, of a phase analogous to the natural mineral braunite ($Mn_2O_3(SS)$) but with SiO_2 contents varying from 0 to approximately 35 wt. %.

Chemical composition and optical properties of the various manganese minerals occurring as phases in the present investigation have been reported in numerous papers and in mineralogy texts, such as for instance Dana's System of Mineralogy (1944).

EXPERIMENTAL METHOD

General Procedure

The quenching technique was used throughout this investigation. Premelted mixtures of oxides were heated at chosen constant temperatures and chosen atmospheric conditions until equilibrium was reached among gas and crystalline phases. The samples were then quenched rapidly to room temperature and the phases present determined by microscopic and x-ray examination.

Starting Materials

The mixtures used in this investigation were made from reagent grade oxides. "Baker Analyzed" MnO_2 was the source of manganese oxide, and "Baker Analyzed" Silicic Acid was the source of silica. The latter was ignited at 1300°C . for 24 hrs. before use. Stock batches were prepared by weighing these materials in desired proportions, carefully grinding and mixing and slowly heating in air to temperatures above the liquidus. After crushing to minus 100 mesh these quenched liquids served as starting materials for the equilibration runs. In a number of experiments the attainment of equilibrium was checked by using as starting materials samples prepared by crystallizing these quenched liquids at controlled temperature and O_2 partial pressure. Two such samples, containing the phases present on opposite sides of a phase boundary curve, were equilibrated side by side to make sure that the reaction would proceed in both directions across the boundary.

Control of Atmosphere

The desired O_2 partial pressure of the atmosphere was attained by mixing O_2 and N_2 gases in required proportions. The O_2 was taken directly from a cylinder of high purity gas (Matheson, purity $\geq 99.6\%$), while the N_2 cylinder gas was purified by passing over copper gauze kept at approximately 600°C ., and subsequently through drying towers containing commercial drying agents ("Drierite"). A gas mixer working on the same principle as that described by Darken and Gurry (1945) and later used in previous studies in our laboratories (Muan, 1955; Muan and Osborn, 1956) was used to control the gas flow to the furnace. The rate of flow of each gas was measured separately through pre-calibrated capillaries in two differential flow meters. The gases were then mixed in a large container, and the gas mixture was passed through a third manometer measuring the total flow of gas into the furnace. The rate of flow was maintained at approximately 0.15 cu. ft. per hour, corresponding to a linear rate of flow of approximately 1 cm. per sec. through the furnace tube.

Furnaces and Temperature Control

The quenching experiments were carried out in a vertical platinum-wound tube furnace. A gas tight high temperature porcelain tube was inserted inside the heating element and protruded above and below the furnace shell. The top of the porcelain tube was provided with a gas-tight watercooled brass head into which sample holder and thermocouple protection tube could be clamped in gas tight connection. The lower end of this tube was provided with a metal container in gas-tight connection with the tube. The gas was introduced into the lower end of the porcelain tube and escaped at the top, through a bottle containing a small amount of sulfuric acid. In this way a slight overpressure (3–4 mm. Hg.) over atmospheric was maintained in the furnace. The samples were contained in small envelopes made of thin platinum foil. No visible contamination of the platinum with manganese was experienced at the relatively high O_2 partial pressures ($> 10^{-2.5}$ atm.) used in this investigation. (Such contamination has been observed at much lower O_2 partial pressures.*) After equilibrium was reached, the samples were quenched rapidly by letting them fall into this cup without disturbing the atmosphere in the furnace. This was accomplished by electrically melting off a thin platinum wire from which the samples were suspended.

The temperature of the furnace was controlled by a platinum-90% platinum 10% rhodium thermocouple inserted close to the hot spot of the furnace and connected to a commercial electronic control device. Actual temperatures in the furnace were measured before and after each run with a second platinum-90% platinum 10% rhodium thermocouple. This was calibrated against melting points defined as follows: Au, 1063° C.; $LiSiO_3$, 1201° C.; $CaMgSi_2O_6$, 1391.5° C.

Examination of Quenched Samples

The identity of phases present in quenched samples was determined by x-ray methods and by examination under a petrographic microscope. The x-ray work was carried out on a Norelco spectrometer unit with Fe radiation.

RESULTS

Results of quenching experiments carried out at various O_2 partial pressures are presented in Table I and shown graphically in Fig. 1. Heavy solid lines in this diagram are curves approximately passing through points (solid dots) representing experimentally determined values of O_2 partial pressures and temperatures for equilibrium coexistence of three crystalline phases and a gas phase in univariant situations in the

* W. C. Hahn, Jr., personal communication.

TABLE I. RESULTS OF EQUILIBRIUM STUDIES

Total Comp. of Mixture (Wt. %)		Temp. of Quench Run	Log p_{O_2} (Atm.)	Phases Present*
Mn ₃ O ₄	SiO ₂			
55.0	45.0	1,160 1,152	0	R+S (tr.) B+S
55.0	45.0	1,122 1,113	-0.20	R+S (tr.) B+S
80.0	20.0	1,204 1,197	-0.40	M+R M+B
55.0	45.0	1,095 1,082	-0.40	R+S (tr.) B+S
55.0	45.0	1,051 1,045	-0.70	R+S (tr.) B+S
71.0	29.0	1,206 1,202 1,170 1,166	-0.70	T M+R M+R B+R
71.0	29.0	1,189 1,185	-0.80	T M+R
71.0	29.0	1,163 1,151 1,141 1,136	-1.00	T H+R H+R B
71.0	29.0	1,131 1,124 1,115	-1.20	T H+R B
71.0	29.0	1,098 1,095	-1.40	T B
71.0	29.0	1,080 1,071	-1.58	T B+H
64.0	36.0	1,053 1,043 1,040	-2.00	T+R T+R+B B+R
71.0	29.0	1,034 1,022	-2.00	T B+H
71.0	29.0	1,005 991 981 973	-2.50	T T T H+B
64.0	36.0	1,005 991 981	-2.50	T+R T+R+B B+R

* Abbreviations used have the following meanings: H=crystals of hausmannite (=tetragonal Mn₃O₄); M=crystals of cubic Mn₃O₄; T=crystals of tephroite (2MnO·SiO₂), R=crystals of rhodonite (MnO·SiO₂(SS)); B=crystals of braunite (Mn₂O₃(SS)); S=crystals of silica (tridymite, SiO₂); tr.=trace.

ternary system Mn-Si-O. These curves have been extrapolated as straight lines (dashed) down to lower temperatures in order to indicate approximate locations of these equilibria in a region where experimental studies are difficult to carry out. Light solid lines in the same diagram illustrate for comparison relations between O_2 partial pressure and temperature for equilibria among gas and two condensed phases (2 crystalline or 1 crystalline and 1 liquid) in univariant situations in the binary system Mn-O, based on recent data of Hahn and Muan (in press) and by Coughlin (1954). It is to be noted that the curve representing the Mn_3O_4 /MnO equilibrium in the binary system also will represent the conditions for equilibrium coexistence of the three condensed phases Mn_3O_4 , MnO and liquid in the system Mn-Si-O if no silica gets into the structure of Mn_3O_4 or MnO.

The data contained in Table I and Fig. 1 can be summarized in the equations below, representing relations of O_2 partial pressure and temperature for the following univariant situations in the system Mn-Si-O:

Mn_2O_3, Mn_3O_4	$:\log p_{O_2} = 8.05 - 10,100 \cdot 1/T$
Mn_3O_4, MnO	$:\log p_{O_2} = 13.31 - 26,000 \cdot 1/T$
MnO, Mn	$:\log p_{O_2} = 7.65 - 40,700 \cdot 1/T$
Mn_3O_4 , tephroite, braunite	$:\log p_{O_2} = 10.08 - 15,700 \cdot 1/T$
Mn_3O_4 , tephroite, rhodonite	$:\log p_{O_2} = 8.25 - 13,200 \cdot 1/T$
Mn_3O_4 , braunite, rhodonite	$:\log p_{O_2} = 13.18 - 20,000 \cdot 1/T$
Braunite, tephroite, rhodonite	$:\log p_{O_2} = 12.48 - 19,000 \cdot 1/T$
Braunite, rhodonite, tridymite	$:\log p_{O_2} = 8.56 - 12,200 \cdot 1/T$

Heats of oxidation for the reactions represented by these univariant equilibria can be calculated from the slopes of the curves in Fig. 1, as follows:

$2MnO \cdot SiO_2 + O_2 = Mn_3O_4 + Mn_2O_3(SS);$	$\Delta H = 72,000 \text{ cal.}$
$2MnO \cdot SiO_2 + O_2 = Mn_3O_4 + MnO \cdot SiO_2(SS);$	$\Delta H = 60,000 \text{ cal.}$
$MnO \cdot SiO_2(SS) + Mn_3O_4 + O_2 = Mn_2O_3(SS);$	$\Delta H = 91,000 \text{ cal.}$
$2MnO \cdot SiO_2 + MnO \cdot SiO_2(SS) + O_2 = Mn_2O_3(SS);$	$\Delta H = 87,000 \text{ cal.}$
$MnO \cdot SiO_2(SS) + O_2 = Mn_2O_3(SS) + SiO_2;$	$\Delta H = 56,000 \text{ cal.}$

These equations are not balanced because solid solution crystals of variable compositions are involved in the equilibria. The heats of oxidation given are for reactions in which 1 mol of O_2 is consumed, and are average values in the temperature interval for which the curves in Fig. 1 have been drawn.

The diagram in Fig. 1 has the shortcoming that it does not show the compositions of the three condensed phases coexisting along the univariant lines or of the two condensed phases coexisting in the areas between the univariant curves. A supplementary diagram is presented in Fig. 2 to show the phase relations as a function of total composition (manganese

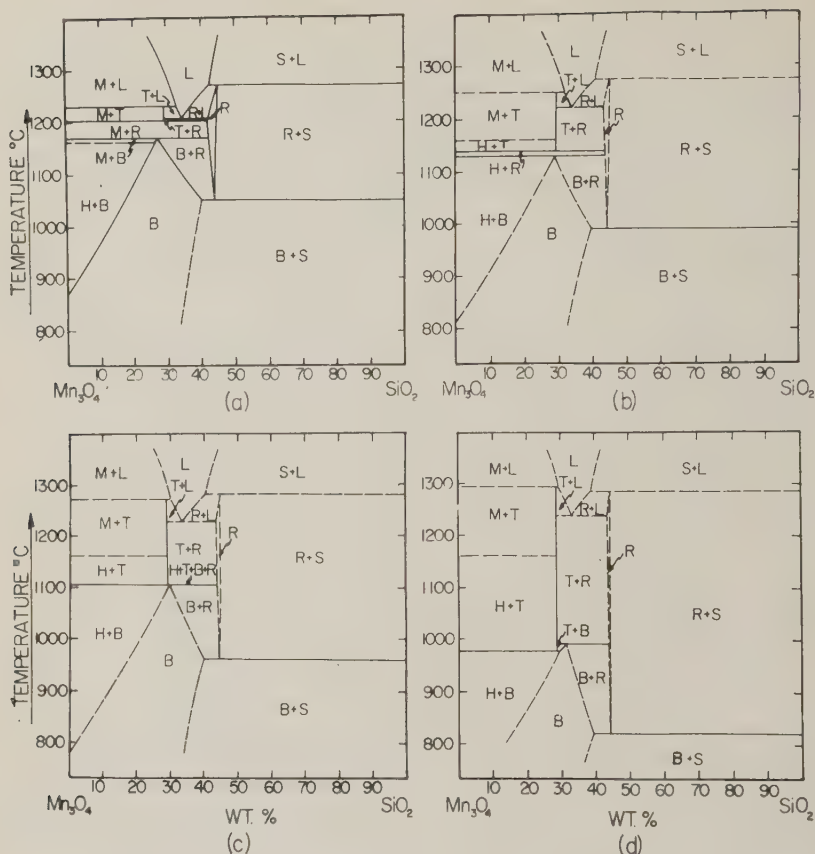


FIG. 2. Diagrams showing phase relations at various levels of O_2 partial pressure in the system Mn-Si-O. The diagrams, labeled *a* through *d* are plotted for O_2 partial pressures of $10^{-0.7}$, $10^{-1.1}$, $10^{-1.35}$ and $10^{-2.5}$ atm., in that order. They are in reality projections of ternary relations into the chosen join Mn_3O_4 - SiO_2 . The diagram in *c* is exceptional in that it shows phase assemblages present at the O_2 pressure ($10^{-1.35}$ atm.) corresponding to a ternary subsolidus invariant situation in the system Mn-Si-O. In addition to the abbreviations used in Fig. 1, the following have been used in this diagram: M=cubic Mn_3O_4 ; H=hausmannite (tetragonal Mn_3O_4).

oxide to silica ratio) of the mixtures at various levels of O_2 partial pressures. The sequence of phase changes occurring as O_2 partial pressure is lowered from that of air to $10^{-2.5}$ atm. can be followed by inspection of the sketches in Fig. 2*a* through *d*, in that order.

DISCUSSION

The data obtained in the present investigation confirm previous observations (Goldschmidt, 1954) of the high stability of Mn^{2+} -containing

phases as compared to those where manganese is present only in higher valence states. Of all phases where manganese is present essentially as Mn^{2+} , the oxide itself, MnO (manganosite), is of course the least resistant to oxidation. It will be observed that MnO does not occur as a phase at the combinations of O_2 pressure and temperature used in the present investigation. In tephroite, $2\text{MnO} \cdot \text{SiO}_2$, the Mn^{2+} is considerably better screened because of the presence of SiO_2 in structure. This phase therefore appears under our experimental conditions, but only at relatively moderate O_2 pressures. In air this phase is stable only in the temperature interval from 1230°C. down to 1204°C. At the latter temperature it oxidizes to the phase assemblage Mn_3O_4 plus rhodonite ($\text{MnO} \cdot \text{SiO}_2$ (SS)). The Mn^{2+} in these phases is somewhat better screened than in tephroite, and they persist to considerably lower temperatures before oxidation takes place. For instance, rhodonite is stable down to 1048°C. (Muan, in press) and pure Mn_3O_4 is stable down to 877°C. in air (Hahn and Muan, in press). However, these phases do not exist *together* in equilibrium down to these temperatures in air. Instead an intermediate phase, here designated Mn_2O_3 (SS), is formed. This phase seems to be analogous to the natural mineral braunite, and probably contains some of its manganese in the divalent state. (For a discussion of this problem, the reader is referred to a recent paper by Muan (in press), where previous literature has been surveyed.) This Mn^{2+} is apparently well screened in the structure, and the phase probably persists stably down to low temperatures.

It is interesting to compare quantitatively the reduction-oxidation equilibria of manganese with those of iron in minerals for which reliable data are now available. An attempt to do this is illustrated in Fig. 3, which shows curves relating O_2 partial pressure and temperature for univariant subsolidus equilibria in parts of the systems Fe-Si-O and Mn-Si-O. In the case of the binary subsystems Fe-O and Mn-O these equilibrium situations are characterized by the coexistence of two condensed phases and gas, while in the ternary systems three condensed phases and gas are present together in equilibrium under conditions represented by the appropriate curves as labeled in Fig. 3. In order to orient the reader, two additional curves are included in Fig. 3, showing relations of O_2 partial pressure and temperature for pure CO_2 and pure H_2O , two of the most important species of the gas phase present in rock systems. One characteristic difference between the patterns of the Mn curves and the Fe curves is recognized immediately: the Mn curves are more "spread out." While MnO is reduced to Mn only at O_2 pressures significantly lower than those at which "FeO" is reduced to Fe, MnO persists as a phase to much higher O_2 pressures than "FeO," and likewise Mn_3O_4 resists oxidation to Mn_2O_3 much better than Fe_3O_4 (magnetite) to Fe_2O_3

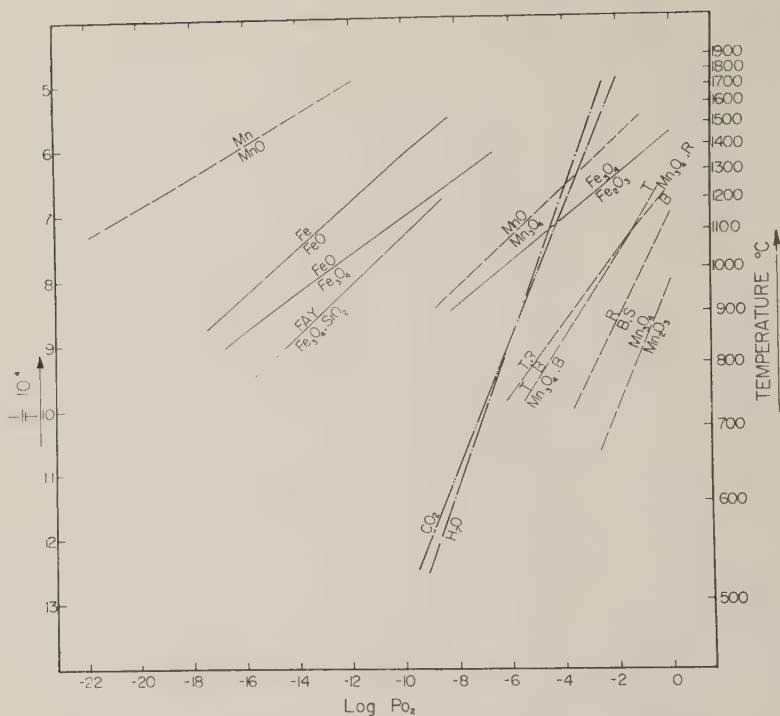


FIG. 3. Diagram presented in order to compare stability relations among various manganese and iron minerals as a function of temperature and O_2 partial pressure. Solid lines represent univariant equilibria in the systems Fe-O and Fe-Si-O, and dash lines represent those in the systems Mn-O and Mn-Si-O. In addition, two lines are drawn to show the O_2 pressure as a function of temperature for the gases H_2O (dash-dot line) and CO_2 (dash-double dot line), as discussed in the text. Abbreviation not explained in previous diagrams has the following meaning: Fay.=fayalite ($2FeO \cdot SiO_2$).

(hematite). These observations of course are equivalent to the statement that Mn^{2+} is exceptionally stable as compared to Fe^{2+} . Another characteristic difference between the behavior of Mn^{2+} and Fe^{2+} is the much greater stabilizing effect of SiO_2 in the case of the former. This is demonstrated by the relatively large distance between the MnO/Mn_3O_4 curve and the curves representing the oxidation of Mn^{2+} silicates, as compared to the situation existing between the FeO/Fe_2O_3 curve and that for oxidation of fayalite ($2FeO \cdot SiO_2$).

The use of the diagram for predicting quantitatively the resistance to oxidation of the various phases represented in Fig. 3 is of course quite simple. Take as an example the situation prevailing at a constant temperature of $1200^\circ C$. Starting with extremely reducing conditions and gradually increasing the O_2 partial pressure, Mn oxidizes to MnO at ap-

proximately $10^{-2.0}$ atm. O_2 and Fe to "FeO" at approximately 10^{-12} atm. at this temperature. As O_2 pressure is increased farther, "FeO" oxidizes to Fe_3O_4 at approximately 10^{-9} atm., and fayalite oxidizes to Fe_3O_4 and tridymite at an O_2 pressure only slightly higher, approximately $10^{-8.5}$ atm. The next phase to yield to oxidation as O_2 pressure increases is MnO, which reacts to form Mn_3O_4 at an O_2 pressure of $10^{-4.5}$ atm. At a p_{O_2} value of approximately 10^{-3} atm. Fe_3O_4 oxidizes to Fe_2O_3 , and at an O_2 partial pressure of $10^{-0.7}$ atm. tephroite oxidizes to rhodonite and Mn_3O_4 . These phases subsequently react at a slightly higher O_2 pressure ($10^{-0.4}$ atm.) to form braunite. Rhodonite oxidizes (to braunite plus silica) only at O_2 pressures above 1 atm. at this temperature.

It should be emphasized that the relations just discussed apply only in the case of the ternary system Mn-Si-O and Fe-Si-O taken separately. For the quaternary system Mn-Fe-Si-O the relations will undoubtedly be drastically different because of extensive solid solution formation among at least some of the phases encountered. The equilibria in such mixed systems could be calculated if we had a quantitative knowledge of the deviation from ideal behavior of the mixed crystals. More experimental data are needed to fill this gap. This work is presently being extended in that direction.

The curves in Fig. 1 representing equilibria where Mn_3O_4 is one of the phases present have a slight change in their slopes at the temperature where the phase transition from tetragonal to cubic Mn_3O_4 takes place (approximately 1160° C., Van Hook and Keith, 1958). However, the heat effect accompanying this transformation is too small to change significantly the straight line relation pictured in the diagram.

The curves shown in Fig. 1 can be extrapolated as straight lines down to lower temperatures and tentative phase diagrams sketched for O_2 partial pressures substantially lower than that prevailing in diagram 2d ($10^{-2.5}$ atm.). It is likely that the subsolidus relations will be similar to that in 2d, except that the horizontal lines indicating the lower temperature limits of rhodonite and tephroite will be shifted downwards. From the curves in Fig. 1 it is estimated that rhodonite is stable down to approximately 500° C. at an O_2 pressure of 10^{-8} atm. and tephroite down to approximately 600° C. under the same conditions.

The intersection at 1104° C. of the two univariant curves in Fig. 1 along which the phases braunite (B), Mn_3O_4 , rhodonite (R), gas, and Mn_3O_4 , rhodonite, tephroite (T), gas, respectively, coexist in equilibrium is an interesting feature of the system. These phase assemblages therefore can exist under equilibrium conditions only at temperatures above 1104° C. and at O_2 pressures above that corresponding to the point of intersection, $10^{-1.35}$ atm. Below this temperature and O_2 partial pressure the

phase assemblages Mn_3O_4 , braunite, tephroite, gas, and braunite, rhodonite, tephroite, gas, respectively, are stable. These relations are easily recognized by an inspection of Fig. 2 together with Fig. 1.

The present data were obtained at a constant total pressure of 1 atm. In order to infer conditions prevailing during formation and alteration of naturally occurring manganese minerals, the effect of elevated hydrostatic pressures must be considered. All equilibria determined in the present study are concerned only with crystalline phases in addition to the gas phase unless extreme pressures are used, the activities of the crystalline phases remain essentially constant, and the curves plotted in Fig. 1 would still apply as a good approximation at elevated hydrostatic pressures if the vertical scale is taken to mean log fugacity values of O_2 instead of $\log p$.

The results of this study seem to offer a promising possibility of inferring some of the conditions prevailing during the formation of manganese minerals. Best known among such deposits are those at Långban in Sweden, which have been described in several papers appearing in the literature (Magnusson, 1924; Flink, 1926; Palache, 1929). A critical analysis of these mineral deposits in view of laboratory data on stability relations established among manganese minerals will be attempted only after the influence of iron oxide and Al_2O_3 on these equilibria has been established. Such studies are presently in progress in our laboratories.

SUMMARY

Stability relations among crystalline phases in the system manganese oxide- SiO_2 have been studied in the temperature interval 973–1206°C. and at O_2 partial pressures varying from $10^{-2.5}$ to 1 atm. Equations relating O_2 partial pressure and temperature for ternary univariant situations have been determined for equilibria involving the phases Mn_3O_4 , braunite (Mn_2O_3 (SS)), tephroite ($2\text{MnO} \cdot \text{SiO}_2$), rhodonite ($\text{MnO} \cdot \text{SiO}_2$ (SS)), and tridymite (SiO_2). Each of these univariant situations is characterized by the coexistence in equilibrium of a gas and three crystalline phases.

A comparison of these data with similar data for iron oxides and fayalite ($2\text{FeO} \cdot \text{SiO}_2$) demonstrates the far greater stability of Mn^{2+} than of Fe^{2+} in common mineral structures. While Mn^{2+} in oxides at high temperatures is reduced to metallic manganese only at O_2 partial pressures far below those sufficient to reduce Fe^{2+} to metallic iron, Mn^{2+} oxidizes to higher valence states only at considerably higher O_2 partial pressures than those necessary to oxidize Fe^{2+} to Fe^{3+} .

The data obtained in the present investigation may perhaps be used to estimate O_2 partial pressure or combination of O_2 partial pressure and

temperature prevailing during formation and alteration of manganese oxide containing mineral deposits. Although the present data were obtained at a constant total pressure of 1 atm., it is expected that the phase relations will remain essentially the same also at somewhat elevated hydrostatic pressures. It is worth noting that the phase assemblage Mn_3O_4 , braunite, rhodonite, gas, and likewise the phase assemblage of Mn_3O_4 , tephroite, rhodonite, gas can exist in stable equilibrium only at temperatures above 1104°C . and at O_2 partial pressures above $10^{-1.35}$ atm. Below this temperature and O_2 partial pressure the phase assemblages Mn_3O_4 , braunite, tephroite, gas or braunite, tephroite, rhodonite, gas are stable.

ACKNOWLEDGMENTS

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REFRACTION, ABSORPTION AND BIABSORPTION IN SYNTHETIC RUBY*

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ABSTRACT

Refractive indices, absorption coefficients, and biabsorption were determined for two synthetic ruby samples, one colored pink by 0.11% Cr_2O_3 and the other colored deep red by 1.40% Cr_2O_3 .

The refractive indices of the pink sample vary from $n_\omega=1.7761$ and $n_e=1.7677$ at 480 μ to $n_\omega=1.7635$ and $n_e=1.7554$ at 700 μ . For the red sample, n_ω and n_e vary from 1.7821 and 1.7741, respectively, to 1.7696 and 1.7614 for the same spectral region.

The maximum value of the absorption coefficient for the ordinary ray occurs at 560 μ for both samples, while the maximum value for the extraordinary ray in both samples occurs at 550 μ . Values of the absorption coefficients at the peak wave lengths are: $k_\omega=34.9\times10^{-6}$, $k_e=25.4\times10^{-6}$ (for the pink ruby) and $k_\omega=311.0\times10^{-6}$, $k_e=138.2\times10^{-6}$ (for the red ruby).

The maximum negative ($k_e < k_\omega$) value of biabsorption for both samples occurs at 570 μ . These biabsorption values calculated from the absorption coefficients are -10.4×10^{-6} and -184.1×10^{-6} for pink and red ruby, respectively. Those obtained by the visual-matching method are -10.0×10^{-6} and -193.0×10^{-6} .

INTRODUCTION

In a recent paper (Mandarino, 1959), an attempt was made to stimulate interest in the quantitative determination of absorption and biabsorption. This paper continues the study with data on these two properties for synthetic ruby. Refractive index data have also been included for the sake of completeness.

Two samples of synthetic ruby were used: a dark red sample containing 1.40% Cr_2O_3 and a pink sample containing 0.11% Cr_2O_3 . The chromium contents were determined by Mr. C. O. Ingamells of the Rock Analysis Laboratory, University of Minnesota.

The writer wishes to thank Dr. R. W. Kebler, of the Linde Air Products Company, Indianapolis, Indiana, for furnishing the samples; Drs. N. Kalenda and A. Emory of the Chemistry Department, University of Michigan, for assisting with the Cary spectrophotometer; and especially, Professor R. M. Denning, of the Mineralogy Department, University of Michigan, who directed the study and contributed many helpful suggestions. The study was supported by the Office of Naval Research.

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TABLE 1. REFRACTIVE INDICES FOR NATURAL AND SYNTHETIC CORUNDUM MEASURED BY VARIOUS INVESTIGATORS

$\lambda(m\mu)$	Kebler (1955)	Melczer (1902)				Mandarino (1959)			
	Synthetic corundum-colorless	Natural* blue to colorless		Synthetic** ruby		Synthetic ruby pink		Synthetic ruby red	
		n_{ω}	n_{ϵ}	n_{ω}	n_{ϵ}	n_{ω}	n_{ϵ}	n_{ω}	n_{ϵ}
366.0	1.79354								
434.1	1.78135								
480						1.7761	1.7677	1.7821	1.7741
486.1	1.77551	1.7760	1.7677	1.7803	1.7719				
500						1.7740	1.7658		1.7723
520						1.7724	1.7640		
540						1.7709	1.7626		
560						1.7697	1.7615		
580						1.7684	1.7604		1.7663
589.3	1.76804	1.7686	1.7604	1.7730	1.7647				
600						1.7675	1.7593	1.7732	1.7649
620						1.7664	1.7583	1.7722	1.7641
640						1.7655	1.7575	1.7714	1.7632
656.3	1.76487	1.7653	1.7573	1.7697	1.7612				
660						1.7647	1.7566	1.7704	1.7624
680						1.7640	1.7559	1.7700	1.7619
700						1.7635	1.7554	1.7696	1.7614

* Averages of data from eight crystals.

** Averages of data from five crystals.

REFRACTIVE INDICES

The ordinary and extraordinary indices of refraction for both pink and red synthetic ruby were determined by the method of minimum deviation. A prism was cut from each boule so that the prism edge was parallel to the crystallographic c -axis. This enabled both n_{ω} and n_{ϵ} to be measured directly.

Table 1 contains the values of n_{ω} and n_{ϵ} for both crystals. Also included in the table are data from Kebler (1955), for n_{ω} in colorless synthetic corundum measured by the American Optical Company; and Melczer (1902), from whom the data in *Dana's System of Mineralogy* by

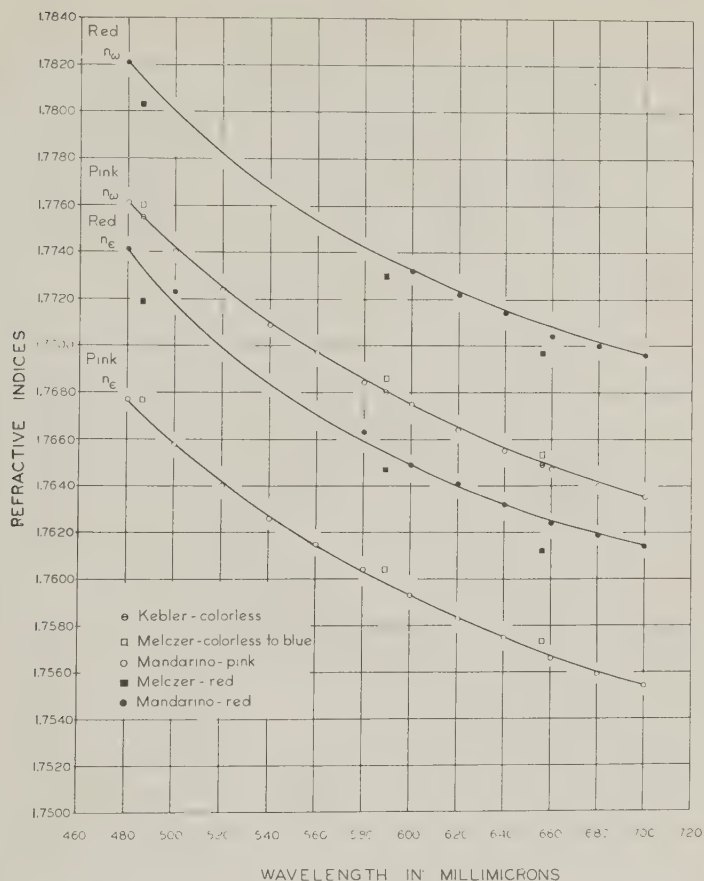


FIG. 1. Refractive indices of natural and synthetic corundum of various colors.

Palache et al. (1944) were taken. It should be pointed out that Melczer's data for blue and colorless corundum are averages of the data from eight natural crystals. Melczer's slightly higher values, also mentioned by Palache et al. (page 526, footnote 18), are for synthetic ruby.

The data from Table 1 are presented graphically in Fig. 1. It can be seen that the refractive indices for colorless, blue, and pink corundum (both natural and synthetic) are almost equal. The deeper red varieties, however, have distinctly higher refractive indices.

The measured values of the refractive indices of pink and red synthetic ruby are considered accurate to within ± 0.0002 for the spectral region 700 $m\mu$ to 600 $m\mu$, and ± 0.0005 for wave lengths below 600 $m\mu$. In red synthetic ruby the values of n_w for the spectral region 500 $m\mu$ through 580 $m\mu$ could not be measured because of the high absorption of the

TABLE 2. HARTMANN CONSTANTS FOR PINK AND RED SYNTHETIC RUBY

Hartmann Constants	Pink Synthetic Ruby		Red Synthetic Ruby	
	n_ω	n_ϵ	n_ω	n_ϵ
n_o	1.7475	1.7399	1.7578	1.7507
c	79.57	76.88	50.40	43.18
λ_o	202.1	203.2	272.5	295.2

ordinary ray in this region. Likewise, n_ϵ could not be measured between 520 $m\mu$ and 560 $m\mu$.

As can be seen from Fig. 1, the dispersion of n_ω and n_ϵ with respect to wave length is normal for both pink and red synthetic ruby. The dispersion for all four sets of data can be expressed by the Hartmann dispersion equation (Hardy and Perrin, 1932):

$$n_\lambda = n_o + \frac{c}{\lambda - \lambda_o} \quad (1)$$

Table 2 lists the Hartmann constants n_o , c , and λ_o for all four indices. Table 3 compares the measured values of n_ω and n_ϵ for both crystals with the values calculated from Equation 1 and the constants of Table 2. In general, the measured and calculated values are compatible, within the probable error of the measurements.

The reciprocal dispersion ν (Hardy and Perrin, 1932) was calculated from:

$$\nu = \frac{n_D - 1}{n_F - n_C} \quad (2)$$

For the pink ruby, $\nu_\omega = 72.5$ and $\nu_\epsilon = 74.5$. The values of ν_ω and ν_ϵ for the red ruby are, respectively, 69.7 and 69.6. Kebler (1955) found $\nu_\omega = 72.2$ in colorless synthetic corundum.

ABSORPTION COEFFICIENTS

The values of the ordinary and extraordinary absorption coefficients for pink and red synthetic ruby were calculated from measurements made with a Cary spectrophotometer. A complete description of the Cary spectrophotometer can be found in a paper by Tarrant (1953). Briefly, the instrument is a recording spectrophotometer employing photoelectric tubes to measure optical density ($D = \log_{10} I_o/I$). The instrument is a comparison-type spectrophotometer; i.e., two optical paths are used, one containing the sample and the other acting as a reference path. A "balancing" circuit makes it possible to trace a curve of constant optical density for a given spectral region before the sample is inserted.

TABLE 3. MEASURED AND CALCULATED REFRACTIVE INDICES OF PINK AND RED SYNTHETIC RUBY

$\lambda(\text{m}\mu)$	Pink				Red			
	n_ω		n_ϵ		n_ω		n_ϵ	
	meas.	calc.	meas.	calc.	meas.	calc.	meas.	calc.
480	1.7761	1.7761	1.7677	1.7677	1.7821	1.7821	1.7741	1.7741
500	1.7740	1.7742	1.7658	1.7658		1.7800	1.7723	1.7718
520	1.7724	1.7725	1.7640	1.7642		1.7782		1.7699
540	1.7709	1.7710	1.7626	1.7627		1.7766		1.7683
560	1.7697	1.7697	1.7615	1.7614		1.7753		1.7670
580	1.7684	1.7686	1.7604	1.7603		1.7742	1.7663	1.7659
600	1.7675	1.7675	1.7593	1.7593	1.7732	1.7732	1.7649	1.7649
620	1.7664	1.7665	1.7583	1.7583	1.7722	1.7723	1.7641	1.7640
640	1.7655	1.7656	1.7575	1.7575	1.7714	1.7715	1.7632	1.7632
660	1.7647	1.7649	1.7566	1.7567	1.7704	1.7708	1.7624	1.7625
680	1.7640	1.7641	1.7559	1.7560	1.7700	1.7702	1.7619	1.7619
700	1.7635	1.7635	1.7554	1.7554	1.7696	1.7696	1.7614	1.7614

To confine each measurement to a particular vibration direction, a polar must be placed in the sample path. A sheet of Polaroid was used for this purpose. The polished ruby plates (cut parallel to the c -axis) were mounted in rotatable holders so that each vibration direction of the plates could be made parallel to the vibration direction of the polar.

With only the polar in the sample path, the instrument was balanced for an arbitrary optical density reading of 1.00 ($I/I_0=0.100$). After balancing, an optical density curve was obtained for the polar alone. The curve covered the spectral region 440 $\text{m}\mu$ to 700 $\text{m}\mu$. Values from this curve were converted to values of I_0 and were found to deviate very little from a value of 0.100. Next, the pink ruby plate was placed in the sample path, and an optical density curve was obtained for the ordinary vibration direction. The ruby plate was then rotated 90° in its own plane, and an optical density curve for the extraordinary vibration direction was obtained. Similarly, curves were recorded for the ordinary and extraordi-

TABLE 4. VALUES OF I_{ω}/I_o AND I_{ϵ}/I_o FOR THE SPECTRAL REGION
440 m μ -700 m μ

$\lambda(\text{m}\mu)$	Pink Ruby ($t=0.302$ cm.)		Red Ruby ($t=0.073$ cm.)	
	I_{ω}/I_o	I_{ϵ}/I_o	I_{ω}/I_o	I_{ϵ}/I_o
440	.108	.102	.053	.047
450	.142	.138	.139	.130
460	.160	.159	.219	.229
466	—	—	.252	.275
469	—	—	.240	.257
470	.172	.171	—	—
473	—	—	.260	.309
476	—	—	.235	.269
480	.175	.180	.248	.309
490	.174	.185	.209	.291
500	.166	.185	.148	.251
510	.153	.180	.092	.200
520	.135	.177	.047	.155
530	.119	.173	.022	.120
540	.105	.171	.012	.102
550	.094	.173	.007	.100
560	.094	.185	.006	.116
570	.102	.204	.008	.155
580	.125	.220	.015	.214
590	.162	.243	.042	.288
600	.209	.265	.109	.350
610	.245	.278	.205	.398
620	.267	.285	.288	.427
630	.282	.294	.335	.437
640	.295	.301	.356	.446
650	.302	.308	.368	.452
660	.309	.315	.365	.452
670	.312	.322	.360	.452
680	.319	.330	.372	.457
690	.328	.337	.356	.457
693	—	—	.332	.452
700	.331	.342	.372	.463

nary vibration directions of the red ruby. The optical density values from these curves were converted (at selected wave lengths) to values of I' . Division of I' values by the predetermined value of I_o (0.100) resulted in values of I'/I_o (the transmittance values uncorrected for reflection losses).

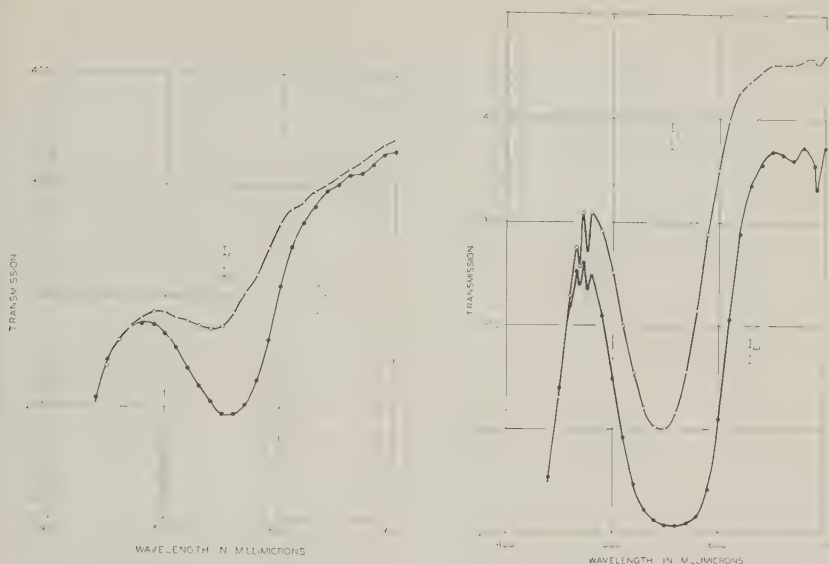


FIG. 2 (*left*). Transmittance of pink synthetic ruby corrected for reflection losses. Sample thickness=0.302 cm.

FIG. 3 (*right*). Transmittance of red synthetic ruby corrected for reflection losses. Sample thickness=0.073 cm.

The corrected transmittance values (I/I_o) for the ordinary and extraordinary vibration directions of both crystals were determined from the values of I'/I_o and n , according to the well-known Fresnel equation for reflection losses. The values of I_ω/I_o and I_ϵ/I_o for pink and red ruby are given in Table 4. These data are also presented graphically in Fig. 2 (pink ruby) and Fig. 3 (red ruby). For certain wave lengths, the red ruby seems to be more transparent than the pink ruby. This can be explained by the difference in thickness of the two samples. The pink ruby was 0.302 cm. thick while the red ruby was only 0.073 cm. thick. Transmittances of media having different chromophore concentrations should not be compared if the media have different thicknesses. Comparison of absorption coefficients of such media is permissible, however, because absorption coefficients are independent of thickness.

The absorption coefficients for the four sets of data were calculated from the following equation:

$$k = - \frac{\lambda \ln(I/I_o)}{4\pi t} \quad \text{Mandarino (1959) (3)}$$

Values of k_ω and k_ϵ for both samples are listed in Table 5, and these data are presented graphically in Fig. 4.

TABLE 5. VALUES OF k_{ω} AND k_{ϵ} FOR THE SPECTRAL REGION
440 m μ –700 m μ

$\lambda(\text{m}\mu)$	Pink Ruby		Red Ruby	
	k_{ω}	k_{ϵ}	k_{ω}	k_{ϵ}
440	25.8×10^{-6}	26.5×10^{-6}	140.9×10^{-6}	146.8×10^{-6}
450	23.2	23.5	96.7	100.0
460	22.2	22.3	76.2	73.9
466	—	—	70.1	65.6
469	—	—	72.8	69.4
470	21.8	21.9	—	—
473	—	—	69.1	60.4
476	—	—	75.0	68.2
480	22.1	21.7	73.0	61.5
490	22.6	21.8	83.5	65.9
500	23.6	22.2	104.0	75.0
510	25.2	23.0	132.6	89.1
520	27.4	23.7	173.2	105.4
530	29.7	24.5	220.0	122.2
540	32.0	25.1	260.0	134.4
550	34.2	25.4	297.0	138.2
560	34.9	24.9	311.0	131.4
570	34.3	23.9	300.0	115.9
580	31.7	23.1	265.0	97.3
590	28.3	22.0	203.6	79.8
600	24.7	21.0	144.6	68.7
610	22.6	20.5	105.3	61.1
620	21.5	20.5	83.8	57.6
630	21.0	20.3	75.2	56.6
640	20.6	20.3	72.0	56.5
650	20.5	20.2	70.8	56.4
660	20.5	20.1	72.6	57.3
670	20.6	20.0	74.6	58.0
680	20.4	19.8	73.3	57.9
690	20.2	19.8	77.6	58.7
693	—	—	83.4	60.2
700	20.4	19.8	75.4	58.8

Several interesting points are illustrated in Fig. 4 and Table 5. In both samples, the absorption peaks for the ordinary ray occur at 560 m μ , while the peaks for the extraordinary ray occur at 550 m μ . (When Vogel (1934) investigated absorption in synthetic and natural ruby, he did not present absorption curves for both the ordinary and extraordinary rays. He did

obtain a composite curve, however, with a peak at $555\text{ m}\mu$.) In general, the absorption curves for both rays in the pink ruby are quite simple. The curves show only one rather poorly-defined absorption band. The absorption curves for both the ordinary and extraordinary rays in red ruby, however, are much more complex. The major absorption band is very sharp and well defined. There are four subordinate absorption bands at $469\text{ m}\mu$, $476\text{ m}\mu$, $670\text{ m}\mu$, and $693\text{ m}\mu$. The band at $670\text{ m}\mu$ is poorly defined. In addition, the $693\text{ m}\mu$ band is sharper for the ordinary ray than

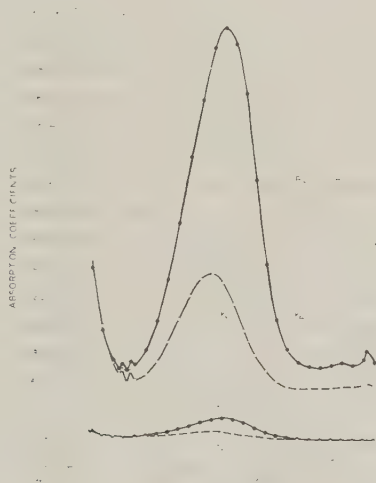


Fig. 4—Absorption coefficients for pink and red synthetic ruby.

for the extraordinary ray; while for the $469\text{ m}\mu$ and $476\text{ m}\mu$ bands, the reverse holds true.

Probably the most striking feature of the curves in Fig. 4 is the extreme difference in pleochroism, or biabsorption ($k_e - k_o$), of the two samples.

An analysis of the probable sources of error indicates that the average total error in the calculated absorption coefficients is about three per cent.

BIABSORPTION

In the preceding section on absorption, the values of the absorption coefficients k_o and k_e for pink and red synthetic ruby were presented for the spectral region $440\text{ m}\mu$ to $700\text{ m}\mu$. Biabsorption values ($k_e - k_o$) can be calculated from the values of k_o and k_e . However, biabsorption can also be measured directly with very little equipment. Biabsorption values for

TABLE 6. VALUES OF BIABSORPTION FOR PINK AND RED SYNTHETIC RUBY DETERMINED VISUALLY AND PHOTOELECTRICALLY

λ ($m\mu$)	Pink Ruby			Red Ruby	
	Visual Photometric Determination		Calculated from k_ϵ and k_ω	Visual Photometric Determination	Calculated from k_ϵ and k_ω
	$t=0.341$ cm.	$t=0.477$ cm.	$t=0.302$ cm.	$t=0.073$ cm.	$t=0.073$ cm.
440	—	—	$+ 0.8 \times 10^{-6}$	—	$+ 5.9 \times 10^{-6}$
450	—	—	$+ 0.3$	—	$+ 3.3$
460	—	—	$+ 0.1$	—	$- 2.3$
470	—	—	$+ 0.1$	—	—
480	$- 0.8 \times 10^{-6}$	—	$- 0.4$	—	$- 11.5$
490	$- 0.8$	—	$- 0.4$	$- 13.5 \times 10^{-6}$	$- 17.6$
500	$- 2.3$	—	$- 1.4$	$- 29.5$	$- 29.0$
510	$- 2.3$	$- 2.7 \times 10^{-6}$	$- 2.2$	$- 52.4$	$- 43.5$
520	$- 3.5$	$- 3.7$	$- 3.7$	$- 73.3$	$- 67.8$
530	$- 4.9$	$- 5.5$	$- 5.2$	$- 95.4$	$- 97.8$
540	$- 7.3$	$- 7.1$	$- 6.9$	$- 127.3$	$- 125.6$
550	$- 9.1$	$- 8.5$	$- 8.8$	$- 165.1$	$- 158.8$
560	$- 10.1$	$- 9.3$	$- 10.0$	$- 194.5$	$- 179.6$
570	$- 9.9$	$- 9.2$	$- 10.4$	$- 193.0$	$- 184.1$
580	$- 8.8$	$- 7.9$	$- 8.6$	$- 164.1$	$- 167.7$
590	$- 4.7$	$- 5.4$	$- 6.3$	$- 113.0$	$- 123.8$
600	$- 2.3$	$- 3.3$	$- 3.7$	$- 63.9$	$- 75.9$
610	$- 1.6$	$- 1.8$	$- 2.1$	$- 30.4$	$- 44.2$
620	$- 0.5$	$- 1.4$	$- 1.0$	$- 24.7$	$- 26.2$
630	$- 0.7$	$- 1.0$	$- 0.7$	$- 21.0$	$- 18.6$
640	$- 0.5$	$- 1.2$	$- 0.3$	$- 18.8$	$- 15.5$
650	$- 0.3$	$- 1.1$	$- 0.3$	$- 13.7$	$- 14.4$
660	—	—	$- 0.4$	$- 7.2$	$- 15.3$
670	—	—	$- 0.6$	—	$- 16.6$
680	—	—	$- 0.6$	—	$- 15.4$
690	—	—	$- 0.4$	—	$- 18.9$
700	—	—	$- 0.6$	—	$- 16.6$

both types of ruby were calculated from the values of I_ω/I_ϵ . These ratios were measured by the double-image method described previously (Denning and Mandarino, 1955; Mandarino, 1959).

Biabsorption measurements were carried out for two specimens: a pink ruby parallelepiped and a red ruby plate. The pink ruby sample provided two dissimilar thicknesses for investigation (0.341 cm. and 0.477 cm.), while the red sample had a single thickness of 0.073 cm.

Values of biabsorption were calculated by substituting the measured values of I_ω/I_ϵ and the appropriate constants in the following equation:

$$k_\epsilon - k_\omega = \frac{\lambda \ln(I_\omega/I_\epsilon)}{4\pi l} \quad (4)$$

These biabsorption values are listed in Table 6 for two thicknesses of pink ruby and one thickness of red ruby. Table 6 also includes the values of biabsorption calculated from the values of k_ϵ and k_ω . Biabsorption

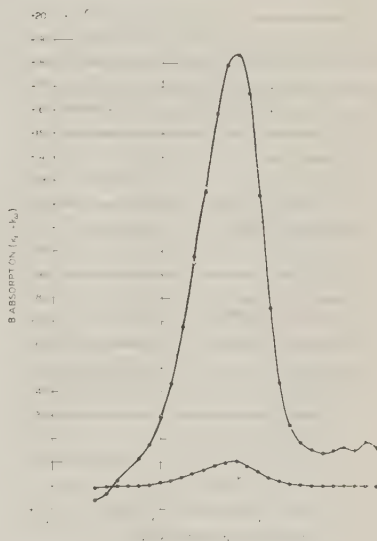
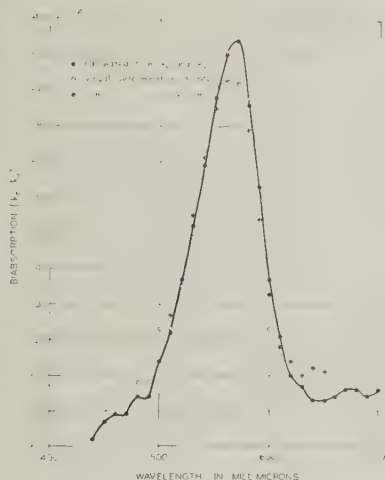


FIG. 5 (left). Biabsorption values for pink synthetic ruby.

FIG. 6 (right). Biabsorption values for red synthetic ruby. Data for pink synthetic ruby from Figure 5 replotted for comparison. Open circles from visual matching method; solid circles from values of k_ϵ and k_ω .

values for pink ruby are plotted in Fig. 5 and those for red ruby are plotted in Fig. 6. Biabsorption values for the pink ruby (calculated from the absorption coefficients) are also included in Fig. 6 for comparison.

It can be seen that the biabsorption reaches a maximum negative value between $560\text{ m}\mu$ and $570\text{ m}\mu$ for both pink and red ruby. There is a striking difference in the values of biabsorption for the two types of ruby, particularly at the peak wave length.

The visually determined values of biabsorption agree quite well with those calculated from the photoelectrically determined values of k_ϵ and k_ω . In the visual determination of biabsorption the greatest source of error occurs in matching the intensities of the images formed by the ordinary and extraordinary rays. Because the errors in the visual match-

TABLE 7. PERCENTAGE ERRORS OF BIABSORPTION VALUES
FOR PINK AND RED SYNTHETIC RUBY

$\lambda(\text{m}\mu)$	Pink Ruby		Red Ruby
	$t=0.341 \text{ cm.}$	$t=0.477 \text{ cm.}$	$t=0.073 \text{ cm.}$
480	40 %	—	—
490	40 %	—	12 %
500	15 %	—	5½ %
510	15 %	9 %	3½ %
520	10 %	7 %	2½ %
530	7½ %	4½ %	2 %
540	5 %	4 %	2 %
550	4 %	3½ %	2 %
560	4 %	3 %	2 %
570	4 %	3 %	2 %
580	4½ %	3½ %	2 %
590	8½ %	5½ %	2 %
600	17 %	9 %	3 %
610	25 %	16 %	6½ %
620	60 %	21 %	8 %
630	60 %	27 %	10 %
640	60 %	27 %	11 %
650	60 %	27 %	15½ %
660	—	—	26 %

ing process are largely psychological, it is difficult to derive equations for them. However, the reproducibility of the measurements can be determined. Over a period of several weeks, seventy-five I_ω/I_ϵ values were determined for each sample at each wave length. A statistical analysis of the resulting data yielded the average values and standard deviations of the measurements. The effect of the error (standard deviation) in I_ω/I_ϵ on biabsorption was then calculated for the samples at each wave length. The resulting errors in biabsorption are listed in Table 7. In the region of maximum biabsorption (530 $\text{m}\mu$ to 590 $\text{m}\mu$) the errors in biabsorption are generally well below 5% and do not exceed 10%.

COMMENTS

The next step in this study might be a correlation of the optical properties with the chromium content. But a correlation based on only two or three* samples would be highly questionable. It should be pointed out, however, that the absorption and biabsorption data for the limited

* The third sample could be considered as pure Al_2O_3 with the absorption coefficients and biabsorption being equal to zero.

range of chromium content presented here do follow Bouguer-Beer's law.

According to Stillwell (1926), corundum takes on a green color when the chromium content becomes high (around 30–45% Cr_2O_3). To the writer's knowledge, no quantitative work has been done through this range. It is hoped that corundum samples with higher chromium contents will become available and thus enable this study to be extended over a wider range of chromophore concentration.

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ELECTRON PROBE ANALYSIS OF MINUTE INCLUSIONS OF A COPPER-IRON MINERAL

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ABSTRACT

An application of the electron probe x -ray microanalyzer to the analysis of extremely minute inclusions in minerals is described. Strongly birefringent grains about 0.03 mm. in size, which resemble what has been termed valleriite, occur in chalcopyrite from the Mackinaw mine, Snohomish County, Washington. These grains were found by the electron probe analysis method to contain about 55 per cent iron and less than 5 per cent copper; the composition was inferred to be approximately FeS. These results suggest that the mineral previously generally termed valleriite in high-temperature copper ores is distinct from the type of valleriite from Kaveltorp, Sweden, and is probably an undescribed sulfide.

INTRODUCTION

During a study of ores from the Mackinaw mine, Snohomish County, Washington (Milton and Milton, 1958), the problem arose of identifying an opaque, strongly birefringent mineral occurring as very fine grains, usually less than 0.03 mm. wide, enclosed in chalcopyrite, CuFeS_2 (Fig. 1). In the past such small grains in many other similar occurrences have been identified as valleriite ($\text{Cu}_{2-3}\text{Fe}_4\text{S}_7$), a platy mineral from Kaveltorp, Sweden (Ramdohr, 1955), although it had never been possible to remove the grains by drilling or other mechanical means so that chemical analyses could be performed. There are indications that the Kaveltorp valleriite and the Mackinaw "valleriite" are entirely different mineral species (Milton and Milton, 1958, p. 432, footnote). The problem seemed ideally suited for the recently developed electron probe x -ray microanalyzer (Castaing, 1951; Birks and Brooks, 1957) with which analysis can be performed on specific areas as small as one micron in diameter on a specimen surface.

INSTRUMENTATION

Several papers on the principles and operation of electron probe instruments have appeared in the literature (Castaing, 1956; Castaing, Philibert, and Crussard, 1957; Cosslett and Duncumb, 1957), therefore, only the briefest description will be given here.

An electron optics system somewhat similar to an electron microscope is used to form a beam of electrons only one micron in diameter. This

beam is allowed to strike a specimen and generate the characteristic x-ray spectra of the elements contained in the one-micron region. An accurate mechanical stage and an optical microscope allow the exact area of interest on the specimen to be positioned in the electron beam for analysis. The characteristic x-rays generated are analyzed by usual x-ray spectrochemical techniques (Birks and Brooks, 1955, 1958; Adler and Axelrod, 1957). That is, the wavelengths of the x-ray lines are used to identify the elements and the intensity of each line is related to the per cent composi-

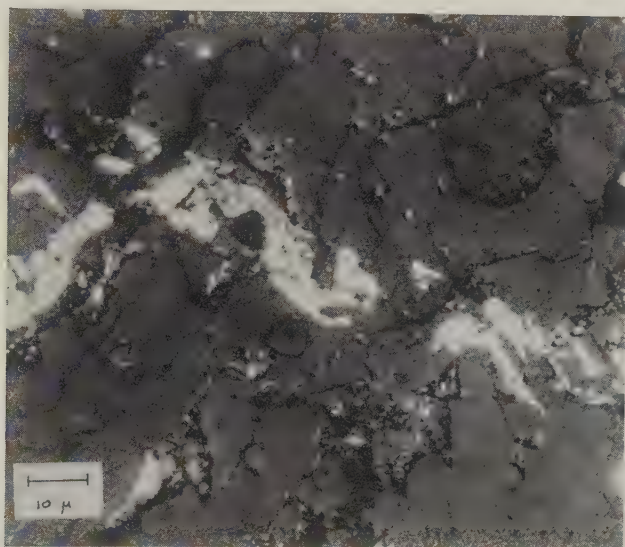


FIG. 1. Photomicrograph showing veins of unknown mineral in chalcopyrite matrix.

tion of that particular element by comparison with standards of known composition.

Figure 2 is a photograph of an electron probe instrument showing the electron optics column with the electron gun at the top, the viewing microscope in front, and several fixed, curved crystals and detectors on the left side (Birks and Brooks, 1955). The fixed crystals and detectors may be replaced by a scanning, curved-crystal spectrometer but for many applications, including the one described herein, it is desirable to measure simultaneously the variation of several elements as the specimen is translated past the electron beam; hence, the several fixed crystals.

SPECIMEN PREPARATION

Examination in the electron probe requires that the specimen surface be flat, smooth, and electrically conducting. A metallurgical type of pol-

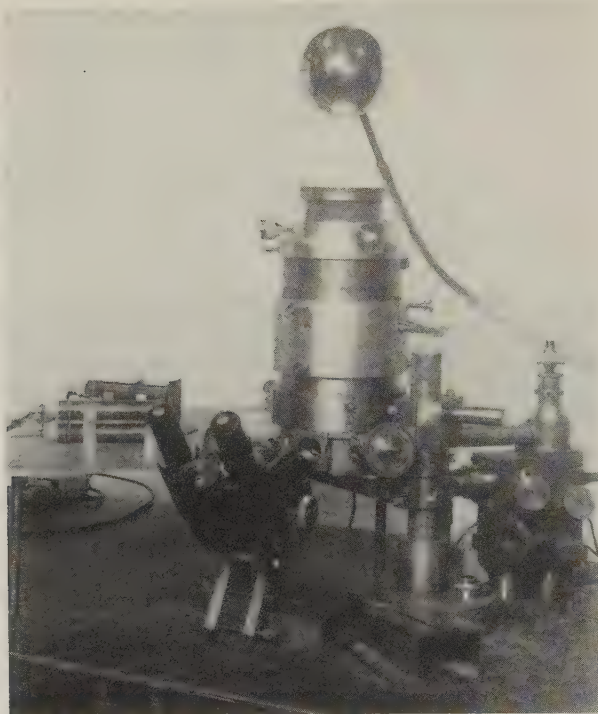


FIG. 2. Electron probe α -ray microanalyzer.

ishing was used to obtain the flat smooth surface on the chalcopyrite and it was made electrically conducting by evaporating a thin layer (100–200 Å) of manganese onto the polished surface. This thin manganese layer does not obscure the gross physical features of the specimen but it does not, of course, allow birefringent areas to be distinguished. Therefore, it was necessary to photograph the specimen in polarized light before the manganese was applied. This allowed the fine grains of interest to be located relative to the gross physical features so that they could be found and measured in the electron probe. Figure 1 shows a photomicrograph of the chalcopyrite mineral containing black gangue areas and the white, lightning-like streaks that are the unknown grains; Figure 1 was taken before manganese evaporation.

For the purpose of comparison, specimens of cubanite (CuFe_2S_3), valleriite ($\text{Cu}_{2-3}\text{Fe}_4\text{S}_7?$), and pyrite (FeS_2) were prepared in a similar manner. All the specimens were placed in the electron probe in a single specimen mount so that intensities from all specimens could be measured without changing any of the experimental conditions.

TABLE 1. ANALYTICAL RESULTS ON SOME CU-Fe MINERALS

Name	Formula	Counts per second		Theoretical Weight per cent		Experimental Weight per cent	
		Fe	Cu	Fe	Cu	Fe	Cu
Chalcopyrite	CuFeS_2	126	160	30.4	34.6	Standard	
Cubanite	CuFe_2S_3	164	98	41.2	23.5	40*	22*
Valleriite (Kaveltoip)	$\text{Cu}_{2-3}\text{Fe}_4\text{S}_7?$	110	120	35.0-38.8	22.1-29.8	26.6*	26*
Pyrite	FeS_2	170	0	46.5	0	Standard	
Unknown (Mackinaw)	About $\text{FeS}?$	212	15-30			51*	0-5*
						58**	0-5**

* Values obtained by comparison with chalcopyrite.

** Values obtained by comparison with pyrite.

RESULTS

The iron and copper x -ray intensities were measured simultaneously by using two crystals and two detectors. Table 1 shows the measured intensities in counts per second for each of the minerals. Chalcopyrite and pyrite were used as standards and the per cent iron and copper in the other minerals calculated by comparison. The per cent concentration of the given element is determined from the relationship that the ratio of the concentrations is directly proportional to the ratio of the measured intensities in counts per second. The agreement of per cent iron and copper in cubanite as calculated from x -ray results and from the known formula is within 1.5 per cent and indicates the precision of the x -ray method. The formula for valleriite is not known accurately but the table shows the nature of the agreement between calculated weight per cent and x -ray measurements for two assumed formulas

The unknown grains may be compared with either chalcopyrite or pyrite and the weight per cent calculated. As shown in the table, the copper content is very low and corresponds to less than 5 per cent in either case. The iron content is 51 per cent if chalcopyrite is used as a standard or 58 per cent if pyrite is used. Because of the observed low copper content, it seems likely that the pyrite standard would be more accurate and that the iron content in the unknown is closer to 58 per cent. Without other evidence it is not possible to ascribe a definite chemical formula to the unknown. If it is assumed to be a sulfide of iron, the formula FeS would give 63.4 per cent iron or a formula of Fe_2S_3 would give 53.8 per cent iron. Since the ordinary Fe_2S_3 is unstable, a formula nearer FeS seems more probable. In fact if the small amount (near 5 per cent) of copper present

is considered as impurity, then a formula approximately FeS agrees rather well with the x -ray observations.

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THE PREPARATION OF SYNTHETIC DOLOMITE

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ABSTRACT

Synthetic dolomite has been formed by precipitation from a solution of $MgCl_2$, $CaCl_2$, and urea subjected to elevated temperatures and CO_2 pressures. The CO_2 pressure is not critical above two or three atmospheres but the temperature must be in the range $200^\circ C.$ – $250^\circ C.$ to obtain dolomite. At lower temperatures basic magnesium carbonate and aragonite are formed, and at higher temperatures the formation of calcite and magnesite is favored. If the temperature is controlled to within $\pm 10^\circ$ of $220^\circ C.$, pure dolomite is precipitated.

The presence of $NaCl$ in the solution extends the range of temperatures over which dolomite can be precipitated. Several other salts have the same effect, and the salt concentration influences the relative amounts of calcite, magnesite, dolomite, etc. which are formed in the precipitates. The influence of the salt is believed to be associated with changes in the activities of the various carbonates in solution.

The pH at which the dolomite precipitations occurred was not measured, but the pH's of the solutions which remained after precipitation were measured at ordinary temperature and pressure and found to be in the range 6.5–7.5.

INTRODUCTION

The synthesis of dolomite has been of interest for many years because of the widespread occurrence of the mineral in nature, both in metamorphic and sedimentary environments. Dolomite has been synthesized by laboratory methods which involve the dry, solid-state, and hydrothermal diffusion of cations in magnesian-calcite mixtures (Graf and Goldsmith, 1955; Graf and Goldsmith, 1956) but there have apparently been no successful attempts to precipitate dolomite directly from solution.* A study has been made of the problem at this Laboratory in connection with efforts to produce pure samples of carbonate minerals for thermoluminescence studies.

DOLOMITE PRECIPITATION

It was found that either calcite or magnesite could be crystallized from chloride solutions under the same conditions of temperature and CO_2 pressure ($120^\circ C.$ – $350^\circ C.$ and 60 atmospheres) by a method similar to that described by Jantsch and Zemek (1949) for the synthesis of magnesite. A $CaCl_2$ or $MgCl_2$ solution is made slightly acidic ($pH = 4$ – 5)

* A method described by Chillingar (1956) for precipitating dolomite from sea water under 4 atmospheres of CO_2 pressure was duplicated by this author without success. The product obtained by this technique contained mostly calcite with a trace of basic magnesium carbonate ($5MgO \cdot 4CO_2 \cdot 5H_2O$) but there were no traces of dolomite. The x-ray powder pattern for basic magnesium carbonate might be easily mistaken for a poorly crystallized dolomite pattern since two of the principal dolomite peaks nearly coincide with two of the basic magnesium carbonate peaks.

and a suitable quantity of urea is added. The solution is placed in an autoclave and raised to the appropriate temperature under CO_2 pressure. The hydrolysis of the urea to NH_3 and CO_2 at elevated temperatures raises the pH sufficiently to precipitate either calcite or magnesite. The proper alkalinity for the optimum crystallinity of the precipitate can be controlled by adjusting the original pH of the solution and the amount of urea added. At a temperature of 350°C . magnesite or calcite is completely precipitated in less than an hour. At lower temperatures, the time required for complete precipitation increases and at 120°C ., 12 to 14 hours are required. At temperatures below 120°C . the method begins to fail because of the exceedingly slow rates of decomposition of the urea. In general, the crystallinity of the samples prepared in short times at high temperatures is as good or better than those prepared over longer periods at low temperatures. The results of the magnesite and calcite precipitations suggested that a mixture of CaCl_2 and MgCl_2 might result in the formation of dolomite under similar conditions.

When the procedure was carried out with a mixed Ca and Mg ion solution dolomite precipitation was found to occur over a narrow range of temperatures near 220°C . In the temperature range from 120°C . to 200°C . poorly crystallized samples of basic magnesium carbonate ($5\text{MgO} \cdot 4\text{CO}_2 \cdot 5\text{H}_2\text{O}$) were obtained, while at temperatures above 250°C . mixtures of calcite and magnesite precipitated. The precipitation of aragonite was observed in the 120 – 150°C . range. At temperatures in the range 200 – 250°C . precipitates containing dolomite, magnesite, calcite and basic magnesium carbonate were formed and if the temperature was carefully controlled at $200^\circ \pm 10^\circ \text{C}$. precipitates of pure dolomite (cf. Fig. 1) were obtained in about three hours. For precipitates containing pure dolomite the yield was fairly low (5–10 per cent).

Variations in the CO_2 pressure had very little effect on the quality (purity, crystallinity, etc.) of the dolomite obtained. Precipitates of well crystallized, pure dolomite were obtained at CO_2 pressures as low as 2 atmospheres and as high as 60 atmospheres.

The composition and crystallinity of all of the precipitates were determined on the basis of their x-ray powder diffraction patterns.

EFFECTS OF NaCl AND OTHER SALTS

To determine what effect the presence of NaCl might have on the dolomite precipitation various concentrations of the salt were added to the initial solution. In general, the effect was to improve the quality of the dolomite crystals and to extend the range of temperatures over which they could be formed. In very dilute and very concentrated salt solutions the precipitation of calcite and magnesite was enhanced.

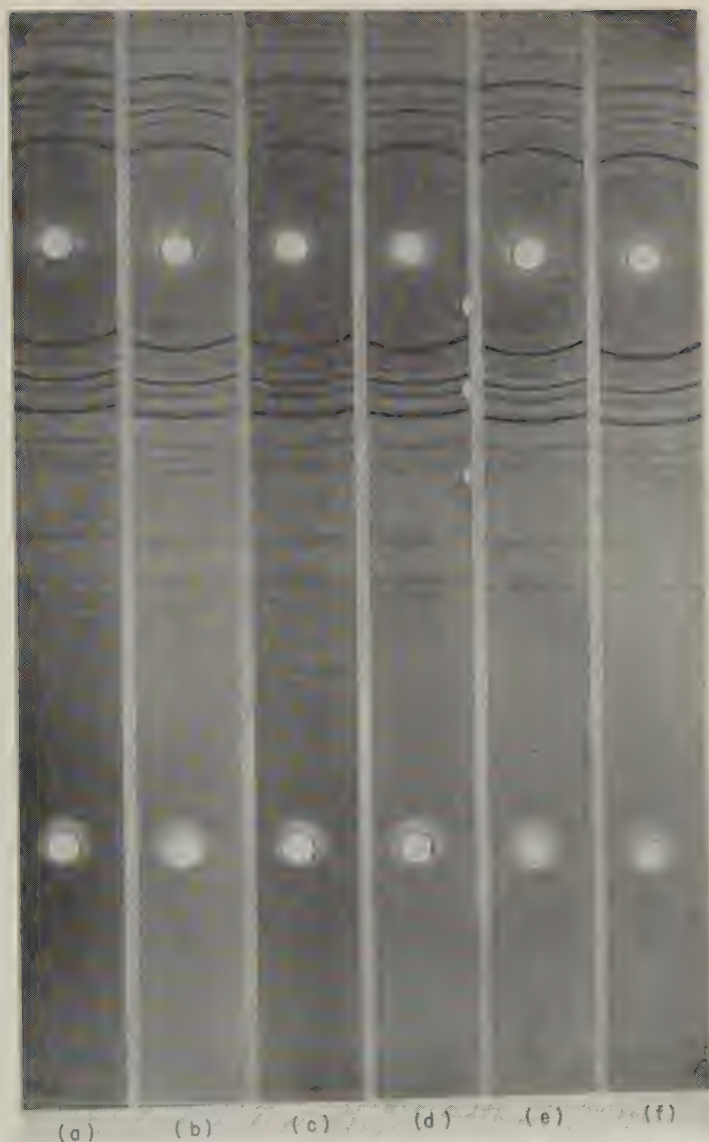


FIG. 1. X-ray powder diffraction patterns for synthetic and natural dolomite samples. All patterns were made with a 4.6 mm. Phillips camera using $\text{CuK}\alpha$ radiation.

- (a) Synthetic sample precipitated without salt.
- (b) Synthetic sample precipitated in presence of NaCl .
- (c) Synthetic sample precipitated in presence of CdCl_2 .
- (d) Synthetic sample precipitated in presence of BaCl_2 .
- (e) Natural dolomite from Ellenburger formation (Texas).
- (f) Natural dolomite from Edwards formation (Texas).

In samples which contained no NaCl, dolomite precipitation was only observed over a range of temperatures between 210° C. and 230° C. At NaCl concentrations of 6–7 per cent, dolomite precipitation was observed over the range 150–350° C. Below 150° C. the formation of aragonite and basic magnesium carbonate was still observed and there was again no trace of dolomite. The high temperature precipitates (230–350° C.) contained magnesite, calcite and dolomite, and the low temperature precipitates (150–210° C.) contained dolomite and traces of basic magnesium carbonate. Pure dolomite could be precipitated only at or near 220° C. Temperatures above 350° C. were not investigated. The time required for complete precipitation at 220° C. was 6–8 hours.

In order to obtain a better understanding of the observed effects of NaCl the precipitations were carried out in the presence of other salts. Dolomite was obtained in the presence of LiCl, KCl, CsCl, CuCl₂, BaCl₂, CdCl₂, ZnCl₂, NaNO₃, NaBr, and Na₂Cr₂O₇ but could not be precipitated in the presence of MnCl₂, SrCl₂, NaI, and CdI₂. To avoid the confusion of mixed ion effects the magnesium and calcium ions were put into solution by dissolving their carbonates in the acid corresponding to the anion of the salt used; for example, when NaBr was used CaCO₃ and MgCO₃ were dissolved in HBr to form MgBr₂ and CaBr₂ in solution.

In most cases the salts which prevented dolomite precipitation also prevented the formation of calcite or magnesite; the precipitates obtained were usually poorly crystallized forms of basic magnesium carbonate (5MgO·4CO₂·xH₂O). Apparently the effects produced by these salts are not associated with the crystal structure favored by the salt since NaCl and NaI both have cubic structures, for example, and NaNO₃ has a rhombohedral structure like dolomite. Moreover, neither the type of salt added (i.e., uni-univalent, uni-divalent, etc.) nor the size of the cation and anion involved appear to be important in influencing the identity of the precipitation products.

The most reasonable explanation for these variations in composition of the precipitate seems to be that they are associated with the changes, caused by the presence of the added salt in the activities (and hence the solubilities) of the various carbonates (calcite, dolomite, magnesite, etc.) in the solution. For it was observed that the composition of the precipitates varied not only with the kind of salt present but also with its concentration. For example, in a group of samples precipitated at 270° C., a solution containing 1.5 per cent NaCl resulted in a precipitate of basic magnesium carbonate; a solution containing 3 per cent NaCl yielded a mixture of the basic magnesium carbonate, calcite and dolomite, while a 7 per cent NaCl solution resulted in a similar mixture with a much greater abundance of dolomite. A solution saturated with NaCl resulted in a mixture of dolomite and magnesite.

The results obtained in NaCl solutions indicate that other salts or salt mixtures might improve the conditions for dolomite precipitation even more. This possibility has not been investigated but it has been observed that of the few salts mentioned above, both BaCl_2 and CdCl_2 improve the quality of the dolomite precipitate a little more effectively than NaCl. Figure 1 compares the x -ray diffraction patterns of dolomite prepared in a solution free of added salts with those for samples obtained in NaCl, BaCl_2 , and CdCl_2 solutions. Patterns for two natural dolomites are also shown.

EFFECT OF VARIATIONS IN THE CA:Mg RATIO IN SOLUTION

It was found that the relative concentrations of calcium and magnesium ions in the original solutions had important effects on the products obtained. The Ca:Mg ratio in solutions which yielded the best dolomite varied with the temperature and the kind of salt present, but was independent of the CO_2 pressure over the range studied. For example, at 220° C. in the presence of NaCl the optimum Ca:Mg ratio (by weight) in solution was 1.4. The Ca:Mg ratio in the best synthetic dolomite samples prepared here was 1.67 (as determined by thermogravimetric analysis) in agreement with the theoretical value, but in the presence of NaNO_3 it was 1.9. At 300° C. with NaCl present the optimum ratio was 2.1 but it was only 1.2 at 170° C. At temperatures above 200° C. the formation of calcite was observed when the Ca:Mg ratio was greater than optimum and magnesite was found when the ratio was less than this. Below 220° C., Ca:Mg ratios greater than optimum favored the formation of basic magnesium carbonate rather than calcite, and Ca:Mg ratios less than optimum favored the formation of both magnesite and basic magnesium carbonate. At 220° C. variations in the Ca:Mg ratio over a fairly wide range did not appreciably affect the quality of the product obtained, which was pure dolomite. These results add significance to the fact that dolomite was obtained at temperatures near 220° C. whether NaCl was present or not, and indicate that the changes in the activities of the carbonates in solution resulting from the different CaCl_2 and MgCl_2 concentrations might be more important than the relative amounts of calcium and magnesium ions in solution.

It was observed from the powder patterns that the d -spacings for the calcite and magnesite in high-temperature precipitates were appreciably different from their normal values. These shifts in the d -spacings (to smaller values for calcite and larger values for magnesite) are probably the result of magnesium substitution in the calcite lattice and calcium substitution in the magnesite lattice (Goldsmith and Graf, 1958). However, there was very little correlation between shifts in the calcite and magnesite spacings and the Ca:Mg ratio in the original solution. In

general, the shifts in the calcite spacings were greater than those in magnesite and the precipitates in which dolomite was found exhibited smaller shifts in the calcite and magnesite *d*-spacings than those which contained only calcite and magnesite (obtained by precipitation at high temperatures without the addition of NaCl).

EFFECT OF UREA CONCENTRATION

The quality of the dolomite was found to be a rather critical function of the amount of urea added to the system. The optimum urea concentration varied with CO₂ pressure (increased with increasing pressure) but not with temperature. It was not possible to measure the pH of the solutions during precipitation in the autoclave, and the pH of the solution which remained after precipitation (measured at room temperature and pressure with a Beckman pH meter) was probably a very poor indication of the pH which existed in the autoclave under high CO₂ and NH₃ pressures.

The final pH values of all of the solutions which contained the best dolomite precipitates were in the range 6.5–7.5. Final pH values which fell within this range were observed over a wide range of original urea concentrations and original acidities, but for a given CO₂ pressure the best dolomite samples were always found in solutions of the same urea concentration. For example, at 60 atmospheres CO₂ pressure the best dolomite precipitates were obtained from solutions containing 3 per cent urea with final pH values in the 6.5–7.5 range. Solutions containing as little as 1 per cent or as much as 6 per cent urea yielded final pH values in this same range (perhaps due to the buffering action of CaCO₃ in the presence of ammonium chloride), but the dolomite in these samples was of much poorer quality and contained other products.

To illustrate the effects of variations in the temperature, salt concentration, Ca:Mg ratio, and urea concentration, some representative results have been selected from the 200 samples which were prepared and these are presented in Table 1. The relative amounts of each product in the precipitate have been roughly estimated from the *x*-ray powder patterns. The Ca⁺⁺ concentration (0.023 g./ml.) and the total volumes (35 ml.) of the original solutions were constant for the samples shown in Table 1.

TEMPERATURE EFFECTS

Fairly conclusive evidence is provided by these experiments that elevated temperatures are necessary for dolomite to be the thermodynamically stable product in the system used here. The lowest temperature at which dolomite could be precipitated was approximately 150° C. and

TABLE 1

Original Solution					Precipitate				
Sample	Ca:Mg	% NaCl	% Urea	Temp.	Dolo- mite	Cal- cite	Magne- site	5MgO· 4CO ₂ ×H ₂ O	Arag- onite
154	1.4	0	2.9	125° C	0	0	0	30%	70%
129	1.4	0	2.9	180° C	0	0	0	100%	0
139	1.4	0	2.9	230° C	100%	0	0	0	0
176	1.4	0	2.9	270° C	30%	0	60%	10%	0
1	2.6	0	2.9	295° C	0	50%	30%	20%	0
19	2.1	1.5	2.9	270° C	0	trace	0	100%	0
20	2.1	3.0	2.9	270° C	20%	20%	0	60%	0
21	2.1	14.0	2.9	270° C	75%	20%	0	5%	0
22	2.1	sat.	2.9	270° C	80%	0	20%	0	0
177	1.4	1.5	2.9	220° C	100%	0	0	trace	0
178	1.4	3.0	2.9	220° C	100%	0	0	0	0
179	1.4	7.1	2.9	220° C	90%	0	0	10%	0
181	1.4	sat.	2.9	220° C	80%	0	0	20%	0
33	2.4	7.1	2.9	220° C	90%	0	10%	0	0
48	1.7	7.1	2.9	220° C	100%	0	trace	0	0
50	1.4	7.1	2.9	220° C	100%	0	0	0	0
52	1.2	7.1	2.9	220° C	80%	0	20%	0	0
59	1.4	7.1	1.4	220° C	50%	0	0	50%	0
60	1.4	7.1	2.9	220° C	100%	0	0	trace	0
61	1.4	7.1	5.7	220° C	60%	0	30%	10%	0
62	1.4	7.1	14.0	220° C	0	40%	40%	20%	0

this lower limit appears to be independent of the CO₂ pressure in the system. This is well above the temperature required for the complete hydrolysis of urea (in the times involved here) at atmospheric pressure and it has been demonstrated by at least two authors (Krase, 1930 and Kawasumi, 1955) that increased CO₂ pressures do not affect the hydrolysis rate.

This point is of interest in connection with attempts to precipitate dolomite under conditions which might have existed during its natural formation in sedimentary environments. The failure to observe its precipitation at temperatures below 150° C. in these experiments does not provide conclusive evidence that it could not be formed at lower temperatures in a different system or over much longer periods of time in this system. The formation of dolomitic sediments in a number of saline lakes

has recently been reported by Alderman and Skinner (1957) in southeast Australia. An investigation of the thermodynamic equilibrium constants associated with the various components of the present system might suggest means of precipitating dolomite in the laboratory at temperatures and pressures more similar to earth-surface conditions.

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RED-LUMINESCING QUARTZ

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ABSTRACT

Red-cathodoluminescent quartz has been synthesized from amorphous silicic acid containing minor amounts of Al^{+3} and Mn^{+2} , in a reducing atmosphere at 1200°C . The emission spectrum shows a band extending from $5400 \text{ \AA}$ to $>7000 \text{ \AA}$, with a maximum $6500 \text{ \AA}$.

INTRODUCTION

During the course of investigating some luminescent glass systems, a red-cathodoluminescent coating was observed on the surface of certain high-silica glass samples. These were prepared in our laboratory by impregnating (Hood and Nordberg, 1943; Nordberg and Rumenapp, 1942; Nordberg and Rumenapp, 1944; Nordberg and Rumenapp, 1944) porous 96% SiO_2 glass (Corning No. 7930) with a solution of a manganese salt and firing at 1200°C . in a reducing (H) atmosphere. The coating was white, and under excitation with a Tesla spark-coil showed red luminescence and some afterglow. The material was not excited by either $2537 \text{ \AA}$ or $3650 \text{ \AA}$ Hg light. X-ray patterns (obtained with a 114.5 mm. cylindrical camera and $\text{CuK}\alpha$ radiation) revealed that the coating was composed of quartz with normal lattice spacings.

The existence of red-luminescing quartz raises several points of interest. (1) First, red-luminescing quartz has never been found in nature, with two doubtful exceptions (Peters, 1930; Saksena and Pant, 1951). (2) Recently, Feldman of the Naval Research Laboratory, working on an independent problem of luminescent thin films on glass, obtained a red-cathodoluminescent film of quartz by thermal evaporation in vacuo of a willemite phosphor (Feldman and O'Hara, 1958). (3) The anomalous generation of quartz at a temperature far above the normal stability range (870°C .) is not unprecedented. Several workers (Schulman, Claffy and Gintner, 1949; Bailey, 1949; Birks and Schulman, 1950) have reported the high-temperature formation of quartz from amorphous silicic acid in the presence of certain elements, such as Ca, which catalyze the reaction. The effectiveness of an aluminum-manganese (both are essential to red-luminescing quartz) combination, however, has not been known.

THE PHOSPHOR—COMPOSITION AND SYNTHESIS

Studies were made of the composition of the fortuitously-occurring material in the attempt to develop a method of controlled synthesis by conventional means. The presence of aluminum as well as manganese

was determined to be essential to the phosphor composition. Aluminum is a minor constituent employed in preparing high-silica glass (Hood and Nordberg, 1940; Hood and Nordberg, 1940; and Hood and Nordberg, 1942). The original luminescent coating apparently resulted from the interaction of an aluminum-bearing glass with the manganese-solution. If the sample is prepared without aluminum ($\text{SiO}_2\text{:Mn}$ only), the x -ray diffraction pattern obtained is predominantly that of cristobalite with only little quartz, and under spark-coil excitation the product shows dim pink emission and no afterglow. If prepared with aluminum alone ($\text{SiO}_2\text{:Al}$), only an amorphous material with weak white cathodoluminescence is obtained.

The phosphor is best prepared from amorphous silicic acid (Mallinckrodt's "Special Bulky") to which Mn^{+2} and Al^{+3} are added as aqueous nitrate solutions. The charge is dried, without mixing, under infrared radiation; fired in air at 1000°C . for one hour; then ground and mixed with a mechanical mortar and pestle; and finally fired at 1200°C . in an atmosphere of hydrogen for one hour. The preliminary air-firing serves to produce higher manganese oxides which mix more readily than the MnO_2 produced during drying. A reducing atmosphere is needed to assure the presence of divalent manganese. The firing temperature is quite critical—at 1100°C ., a yellow-luminescing, probably amorphous, product is obtained; at 1250°C ., the product is inert.

The optimum (molar) composition of the phosphor is: 0.90 SiO_2 , 0.10 MnO , and 0.001 Al_2O_3 . The possible range in activator concentration—of both manganese and aluminum—is very restricted. The upper concentration limit for MnO is approximately 0.10, whereas a lower concentration (0.05 mole) of MnO produces noticeably weaker and whiter emission. The luminescence of compositions containing more (0.005) or less (0.0005 mole) Al_2O_3 is less intense and decays much more rapidly than that of the phosphor of optimum composition. With the view to improving the brightness of the phosphor, several attempts were made to introduce more manganese and aluminum into the quartz lattice by means of fluxes, charge compensating cations, etc., but without success.

The phosphor preparations contain minor amounts of cristobalite and rhodonite (MnSiO_3), according to the x -ray diffraction patterns. MnSiO_3 is known to fluoresce at liquid nitrogen temperature under ultraviolet excitation. Its cathodoluminescence at room temperature, however, is negligible and does not contribute to the brightness of the phosphor. Moreover, the MnSiO_3 and any traces of amorphous silica which may be present are readily leached from the phosphor by treating it with 1% HF at room temperature for one hour. This effects no obvious change in emission brightness or color, although it slightly whitens the color of the

phosphor in reflected light. Digestion with 1% HF for as long as 14 hours, and solution of 80% of the sample, did not lead to preferential leaching of the cristobalite, although Sosman (1927) citing Schwarz (1912) reported a five-fold greater solubility for cristobalite as compared with quartz of uniform particle size. Differences in degree of crystallization and the distribution of the two minerals undoubtedly influence the extent of differential solubility. Since cristobalite is not known to luminesce, it should serve at most to dilute the phosphor and reduce its apparent brightness.

LUMINESCENCE

The phosphor is not excited by 2537 Å or 3650 Å ultraviolet. However, after exposure to x -rays (30 Kv, 15 ma) it phosphoresces salmon pink for several (5–10) minutes' duration, and is also excited to red luminescence and pronounced phosphorescence by 3650 Å; less so by 2537 Å excitation. The response to ultraviolet excitation after x -ray irradiation is a temporary property, and must represent an optical release, via the Mn centers, of energy trapped in the irradiated quartz. This phenomenon—radiophotostimulation—has not been reported previously for the quartz minerals. Audubert, Bonnemay, and Lautout (1950) described blue-white radiophotoluminescence in x -ray irradiated natural quartz. In the latter instance, the irradiation produced permanent centers, and the ultraviolet excitation could be repeated indefinitely.

The luminescence spectrum is reproduced as Fig. 1. It consists of a

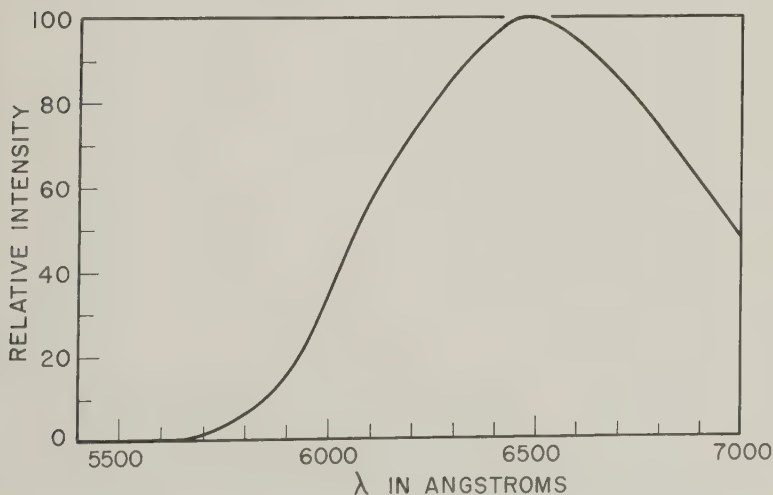


FIG. 1. Emission spectrum, under cathode ray excitation, of red-luminescing quartz.

broad band extending approximately from 5400 Å to beyond 7000 Å, and peaking at 6500 Å. The luminescence has an initial, exponential decay with a decay time of 8 milliseconds. These measurements were made under cathode ray excitation, using a phosphor sample that had been leached with HF. The phosphor also has a long-term afterglow, or phosphorescence, persisting (as detected by eye) for perhaps 5 minutes.

RED-LUMINESCING QUARTZ

The literature of mineralogy contains no reference to red-luminescing quartz. During a recent comprehensive study, Frondel and Hurlbut (1953) inspected some 1816 specimens of quartz and its varieties under 2537 Å and 3650 Å ultraviolet. A very few fluoresced, none red, and the fluorescence was in all cases attributed to foreign *inclusions* and not to the quartz itself. X-ray irradiation of natural and fused quartz excites blue-white fluorescence and phosphorescence, and also produces radiophotoluminescence in response to 2200–5500 Å excitation, according to Audubert et al. (1950).

J. T. Randall (1939), on the other hand, reported that silica (crystal-line state not specified) prepared with 100 p.p.m. manganese by heat treatment at 1400° K. luminesced (4450 Å?, 5600 Å emission bands) under spark-coil excitation at low temperature (90° K.), but that the red emission band of manganese appeared to be missing. At room temperature, only a broad continuum was seen.

Saksena and Pant (1951) reported that the cathodoluminescence of quartz is so feeble that 70,000 V cathode rays and a 6-hour (spectrographic) exposure were necessary to obtain the spectrum, which consisted of two bands, at 3000–4900 Å and 5650–6550 Å. They were inclined to believe that the long wavelength band corresponded to the red cathodoluminescence observed by Peters (1930) and may have been associated with the Si-O bonds in quartz or with F centers produced by the intense irradiation. Certain early workers—Goldstein (1907); Peters (1930)—studying vacuum tube discharges, observed red-fluorescing areas on the tube walls (glass, fused quartz, rock crystal). Peters, using low-voltage cathode rays and 50-hours' spectrographic exposure, obtained a spectrum from pure quartz which consisted of a band at 5895–7238 Å (max. at 6338 Å and 6425 Å) as well as bands in the green (5600 Å) and blue (4790 Å). The red fluorescence disappeared, however, after 70 hours of operation. Peters attributed the fluorescence to the SiO₂ group.

We have examined a few random specimens of quartz with a spark-coil and have found no cathodoluminescence in any. These included rose quartz (Bedford, N. Y.), amethyst (Patterson, N. J.), smoky quartz (locality unknown), drusy quartz associated with pyrite crystals (Lead-

ville, Colo.), crystals from sandstone (Arkansas), and crystals intergrown with hematite (Elba or Frizington?). Synthetic crystals, grown by the Squier Signal Laboratory, Fort Monmouth, N. J., also were inert for the most part, although some had weak blue cathodoluminescence.

It is believed that the red-cathodoluminescent film obtained by Feldman and O'Hara (1958) by evaporation by $\text{Zn}_2\text{SiO}_4\text{:Mn}$ or from SiO_2 plus manganese, and identified by x-ray diffraction and infrared reflection spectra as quartz, developed by a reaction with traces of aluminum in the Vycor glass substrate, and is comparable to the independently prepared phosphor, quartz: (Mn+Al), discussed in the present paper and briefly described elsewhere in a Letter to the Editor (Claffy and Ginther, 1959).

MANGANESE AND ALUMINUM IMPURITIES

Linwood and Weyl (1942) have postulated that the red luminescence of manganese in certain silicate glasses and crystalline compounds may be due to interstitial Mn^{+2} , in 6-fold coordination. Buerger's work (1948) has indicated, however, that only an ion such as Li^+ ($0.60 \text{ \AA}$) is small enough to enter the quartz lattice, and that large ions (Na^+ , $0.95 \text{ \AA}$) can occur only in the cristobalite-type structure. Although Mn^{+2} ($0.80 \text{ \AA}$) is intermediate in size, its charge is greater. Manganese is a rare impurity in natural and synthetic quartz. For example, in ten published spectrographic analyses of quartz, manganese is reported by Cohen and Sumner (1958) as "not found"; and of seven analyses of amethyst (Cohen, 1956), manganese was "not found" in two and its concentration in the other five never exceeded 0.006% . Frondel (1952) reported ten chemical analyses of quartz. Manganese was not found in four; in the remaining six, the highest concentration was 0.00005% . Furthermore, in the growth of synthetic quartz it has been the experience at the Squier Signal Laboratory (J. M. Stanley—private communication to G. W. Arnold, Jr., of NRL; Feb. 20, 1957) that manganese could not be incorporated into the growing crystal.

It is therefore of interest to consider the present case of the phosphor, quartz: (Mn+Al), where optimum luminescence is obtained upon the addition of 10 mole% manganese. We must assume, on the basis of the known behavior of manganese in relation to natural and synthetic quartz, that only some few thousandths of a per cent manganese has been incorporated into the quartz lattice. It may be that in the presence of the aluminum, slightly more manganese can enter the crystal. Probably another, greater, percentage of the manganese has entered the cristobalite since the cristobalite structure is open and readily accommodates large ions (Buerger, 1948; Linwood and Weyl, 1942; Barth and Posnjak,

1932). By chemical analysis it was determined that the leached phosphor—i.e., quartz+cristobalite, actually contained 1.5% (wt.) manganese and the crude, unleached phosphor contained 22.5% MnSiO_3 . Of the initial quantity of manganese used in synthesizing the phosphor, therefore, 96% formed MnSiO_3 and only 4% was incorporated into the quartz and cristobalite lattices. We are forced to conclude, then, that the bulk of the manganese must be fixed as rhodonite in a favored, competing reaction. It is not clear, otherwise, why such a great excess of manganese should be necessary to obtain the phosphor.

Aluminum, in concentrations of 0.0001 to 0.01%, is a common impurity in quartz (Fron del, 1952), and is known to substitute for Si^{+4} in the tetrahedral network of quartz and silicate minerals, the charge imbalance being generally compensated by interstitial alkali ions. Perhaps (Al+Mn) form a similar charge-compensating pair in the quartz phosphor; chargewise, 1 Mn^{+2} could compensate for 2 Al^{+3} ions.

Cohen and Sumner (1958) elaborated the thesis that aluminum can occupy interstitial as well as substitutional positions in the quartz lattice, and that interstitial impurities expand only the *a* lattice direction markedly, whereas substitutional impurities affect both axes. Our *x*-ray diffraction data for the red-luminescing quartz phosphor are not of sufficient precision to distinguish the small lattice changes involved. Quartz containing interstitial aluminum only is said not to develop the 4600 Å absorption band even after extensive (3.8×10^8 r) *x*-ray irradiation (Cohen and Sumner, 1958). A phosphor sample subjected to approximately that dosage by irradiation in a Van de Graaff generator showed slight discoloration. This result in itself is inconclusive since absorption measurements could not be made on the phosphor-powder.

It may be argued that the Mn-bearing cristobalite is actually the active, luminescent phase and inability to separate the quartz from the cristobalite leaves identification of the phosphor unsettled. The following facts are convincing, although indirect, evidence that the phosphor is indeed quartz. (1) The fortuitous luminescent coating on glass is quartz only. (2) The luminescent thin film prepared by Feldman is quartz only. (3) The characteristic red emission is obtained only when (Mn+Al) are used to prepare the phosphor, in which case the *x*-ray diffraction pattern shows predominantly quartz. When manganese alone is used, the product is inert and the *x*-ray diffraction pattern shows cristobalite predominating.

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NICKEL MINERALS FROM NEAR LINDEN, IOWA COUNTY, WISCONSIN*

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ABSTRACT

Nickel minerals occur in comparative abundance as accessories in the Upper Mississippi Valley zinc-lead district of southwestern Wisconsin and northwestern Illinois as well as at other localities in Wisconsin, Illinois, Iowa, Missouri, and Indiana. Millerite is the most common. In southwest Wisconsin millerite is generally associated with violarite and bravoite(?), and near Linden, Wis., all three have been partly altered to a green, yellow, and orange powdery product that is a hydrous basic nickel-iron sulfate, or a series of related sulfates. The alteration product is extremely fine grained and obscurely fibrous; the mean index of refraction is about 1.615 and the birefringence is very low. The x-ray diffraction pattern of the material has broad lines not referable to any known mineral, and chemical analyses indicate that it is essentially a hydrous basic sulfate of nickel and ferric iron.

Millerite was deposited near the end of the main period of deposition of the primary sulfides. The other nickel minerals are probably products of oxidation and secondary enrichment of millerite. A hitherto unrecognized type of symmetrical twinning in millerite, suggestive of a lower symmetry than rhombohedral scalenohedral, is described.

LOCATION AND GEOLOGIC SETTING

Spectroscopic analyses† of mill products from the Venegar Hill Zinc Company's custom mill at Cuba City, Wis. showed notable quantities of nickel and cobalt in ores of the district. This led members of the field party of the U. S. Geological Survey in cooperation with the Wisconsin Geological Survey to search for nickel and cobalt minerals which they first found and collected in 1946. Laboratory investigations of samples from mines near Linden (Fig. 1) showed primary millerite and secondary violarite, bravoite (?) and a hitherto unrecognized hydrous basic sulfate or a series of sulfates of nickel, iron, and cobalt. Although nickel minerals had not been recognized previously in the ore deposits of the Upper Mississippi Valley, U. S. Grant (1905, written communication) had noted green "copper" stains in the Glanville mine at Linden.

The nickel minerals are not common at any locality in the Upper Mississippi Valley zinc-lead district, but are most abundant in the Gilman, Glanville, and Mason mines (Fig. 2). Smaller quantities of millerite and/or violarite have been noted by members of the U. S. Geological Survey at other localities (Fig. 1): (1) James mine, in sec. 9, T.1 N., R. 2 E., near Shullsburg, Wis., (2) Dodgeville No. 2 mine, Dodgeville, Wis., and (3) possibly at the Bautsch mine, 5 miles south of Galena,

* Publication authorized by the Director, U. S. Geological Survey.

† Spectroscopic analyses by J. C. Rabbit, U. S. Geological Survey, March, 1943.



FIG. 1. The Upper Mississippi Valley zinc-lead district showing localities at which nickel minerals have been found. The localities and the nickel minerals identified at each are listed below:

1. Dodgeville No. 2 mine—millerite.
2. Linden area (see Fig. 2 for details)—millerite, violarite, bravoite (2), hydrated nickel iron sulfates.
3. James mine—violarite pseudomorphs after millerite.
4. Farrey mine—violarite and bravoite (?) as pseudomorphs after millerite.
5. Bautsch mine—acicular crystals of millerite.

Ill. Violarite and bravoite (?) as pseudomorphs after millerite were found by Allen F. Agnew of the U. S. Geological Survey at the Farrey mine, along Wisconsin State Highway 11, in the NE $\frac{1}{4}$ NW $\frac{1}{4}$ sec. 14, T. 1 N., R. 1. E., at Leadmine, Wis. (Heyl, Agnew, Lyons, Behre, 1959).

Millerite has a wide distribution elsewhere in the Upper Mississippi Valley, for example: in Lee County, Iowa (Keyes, 1895); in the Chicago, Ill., area (Crook, 1902); from Milwaukee, Wis. (Cleland, 1911, p. 6; Bagrowski, 1940, p. 556-559); in geodes from Iowa and Ill. (Van Tuyl, 1925; Keyes, 1895, p. 401-402); in the St. Louis, Mo., area (Schraut, 1950); in geodes near Columbia, Mo. (Gleason, 1931); and from the Warsaw and Ste. Genevieve limestones of southwestern Indiana (Erd, Evans, Richter, 1957). Bravoite has been found in the Hayden Creek lead mine,

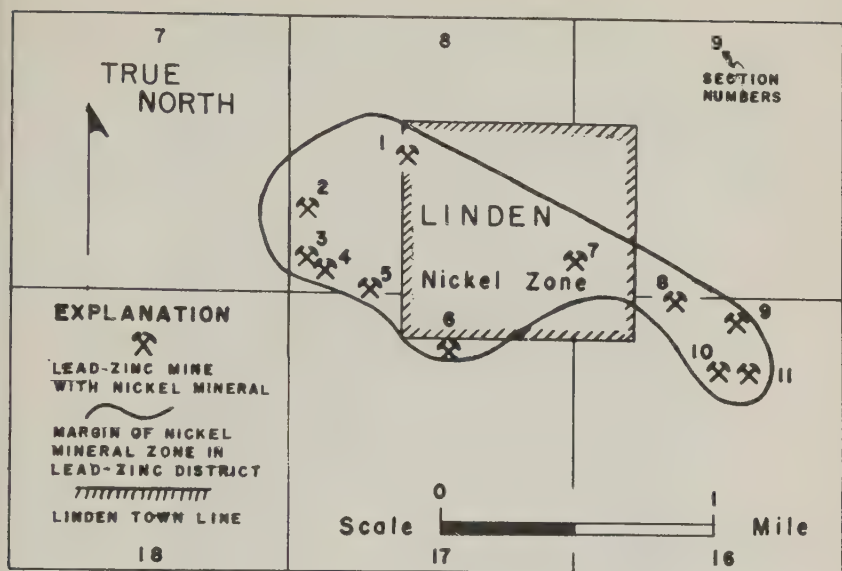


FIG. 2. Zinc-lead mines in the Linden, Wis., area at which the nickel minerals occur. They are most abundant at the Glanville, Mason, and Gilman mines. Brass-yellow millerite was seen only at the Glanville mine, and the green variety of nickel iron sulfates is most abundant there. The mines at which nickel minerals have been found are listed below:

1. Robarts-Hinkel mine.
2. Treglown and Captain Wicks mine.
3. Glanville mine.
4. Linden Open Cut mine.
5. Mason or Linden mine.
6. Optimo No. 2 mine.
7. Dark Horse—Optimo No. 1 mine.
8. East Glanville mine.
9. Ross mine.
10. West Glanville mine.
11. Gilman mine.

southeastern Missouri (Ohle, 1951), and occurs with siegenite, near Fredericktown, Mo. (Rasor, 1943). Millerite with replacement by violarite has recently been identified (1958) by one of the authors, Milton, in Linden County, Mo. associated with galena, sphalerite, chalcopyrite, and barite.

Primary minerals of the ore deposits are quartz (chert and jasperoid), dolomite, pyrite, marcasite (cobaltian), sphalerite, galena, chalcopyrite, barite, millerite, and calcite. Secondary minerals are smithsonite, limonite, cerussite, gypsum, melanterite, chalcocite, covellite, violarite, and

bravoite (?), and the above mentioned sulfate, honessite (Heyl, Milton and Axelrod, 1956). The nickel-bearing zinc-lead ore bodies are groups of banded veins that fill fractures, some of which are faults of small displacement, or are replacements of limestone, shale and dolomite of the Platteville, Decorah, and Galena formations of Middle Ordovician age (Behre, et al., 1950). Near Linden the nickel minerals have been found only in the top member (Quimby's Mill) of the Platteville formation.

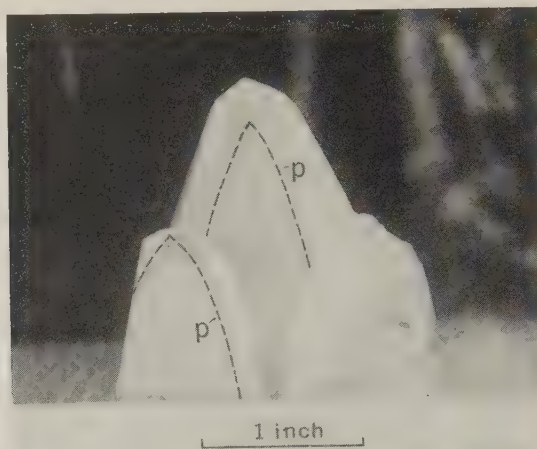


FIG. 3. Calcite habit stage 3 with phantom of stage 2.
Outline of stage 2 phantom at p.

PARAGENESIS OF THE NICKEL MINERALS

The sequence of initial deposition of the primary hydrothermal minerals of the Upper Mississippi Valley zinc-lead district is quartz, dolomite, pyrite, marcasite, sphalerite, galena, barite, chalcopryrite, millerite, and calcite. The period of millerite deposition was short, but extended from that of marcasite to that of the first of four habit stages of calcite.

The four calcite habit stages can be differentiated as follows: (1) the oldest stage is marked by positive and negative rhombohedrons capped by a basal pinacoid; (2) the next stage shows sharp scalenohedrons, with no basal pinacoid; (3) the third stage is distinguished by stubbier scalenohedrons modified by rhombohedrons; 4) the youngest calcite crystals are complex rhombohedrons with vestigial scalenohedrons. Further, each of the successive habit states shows a decreasing degree of etching, and a progressive decrease in cloudiness of the calcite and in the number of sulfide mineral inclusions. Phantoms showing parts of this succession and oriented progressive overgrowths are common (Fig. 3).

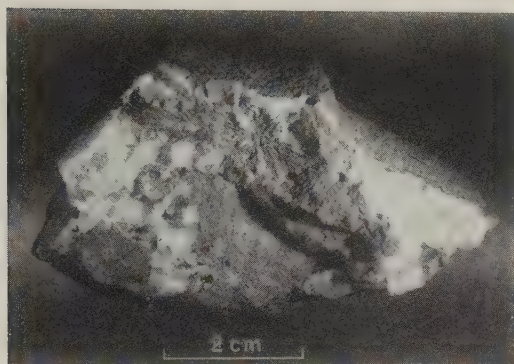


FIG. 4. Radial millerite partly altered to hydrated nickel iron sulfates in calcite on dolomite. In this specimen, the millerite is largely replaced by green, yellow, or reddish-brown nickel iron sulfates.

Radiating acicular clusters of millerite crystals up to an inch in diameter adhere to earlier deposited sulfides. Other clusters are attached to the walls of small fractures in dolomitized limestone breccias. Milk-white coarsely crystallized calcite of the first or second stage usually surrounds the millerite clusters (Figs. 4 and 5). Octahedral galena, marcasite, sphalerite, and chalcopryrite accompany the millerite and its alteration products.

OCCURRENCE OF MILLERITE

Millerite, or pseudomorphs of violarite and bravoite (?) after millerite, form radiating acicular clusters of crystals at all the nickel localities in

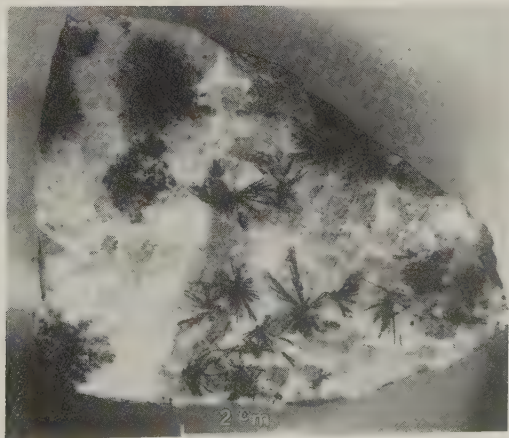


FIG. 5. Radial millerite and violarite in calcite on dolomite. Here the millerite is coated almost completely, as usual, with dark-gray violarite.

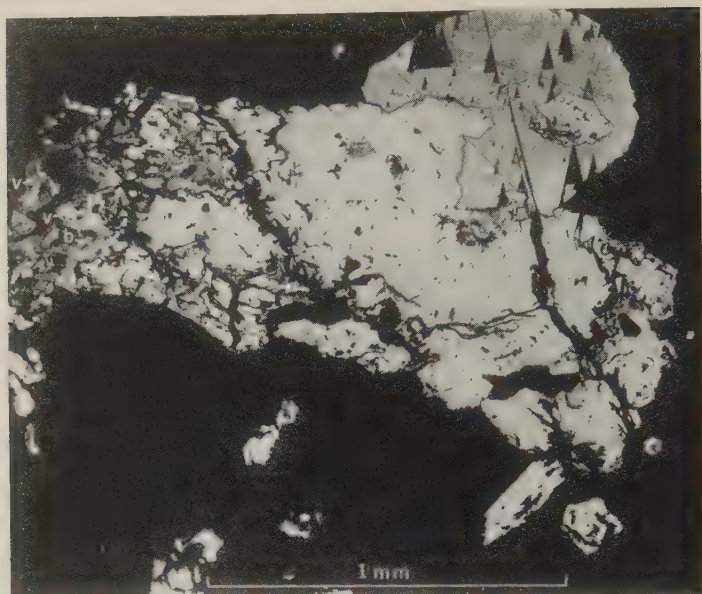


FIG. 6. Polished section showing galena, millerite, violarite and bravoite(?). Galena is in upper right corner (large crescent-shaped grain with triangular pits) and millerite is light gray mineral in most of central area. At left, most of the millerite is altered to slightly darker gray violarite (v) which has prominent cleavage, and to dark gray probable bravoite (b) which is in euhedral pitted grains without cleavage that are surrounded by violarite.

the district. Brassy-yellow millerite is rare; it has been seen only at the Bautsch mine in Illinois, at the Dodgeville No. 2 mine, Dodgeville, Wis. (Fig. 1), and, at the Glanville and Mason mines at Linden, Wis. (Fig 2) where it is partly replaced by violarite. At the other localities the millerite in hand specimens is dark gray-black, though it is unmistakable in polished section. When not completely oxidized, it is usually coated with dark-gray violarite, which is commonly associated with bravoite (?). The relations of these nickel minerals are shown in Fig. 4, 5, 6, 7, 8, and 9.

Millerite occurs as acicular crystal inclusions in bands in calcite, commonly in late calcite of stage one or in early calcite of stage two. The relations of millerite to octahedral galena crystals are shown in Figs. 6 and 7. The youngest galena commonly is in octahedrons, which may be perched upon millerite crystals or enclose them. Rarely is millerite surrounded by a hull of chalcopryrite, as shown in Fig. 12. Chalcopryrite more commonly occurs as bands of small discrete tetrahedrons closely associated with millerite within the first or second stage calcite.

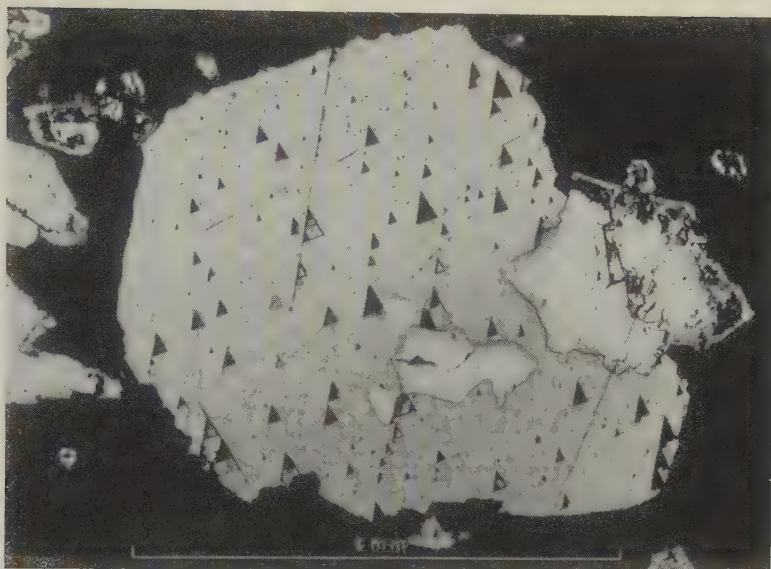


FIG. 7. Polished section showing galena (as triangular pits) with inclusions of millerite. The large irregular grain with sharp projections at right is twinned millerite bordered by a shell of violarite on those sides in calcite (black). In the upper right corner is a hollow shell of violarite within calcite. The violarite has completely replaced millerite except for the central core which was dissolved. In the upper left corner at a is an example of incomplete replacement of this type.

The millerite shows a remarkable symmetrical twinning, not previously noted in the literature (Figs. 8, 9, and especially 10, 11), which suggests a possible lower symmetry than rhombohedral scalenohedral class of the hexagonal system. Buerger (1947) has indicated a similar possibility in the case of dihexagonal dipyrromorphite.

OCCURRENCE OF VIOLARITE AND BRAVOITE (?)

Much of the millerite has been replaced by violarite and bravoite (?). These minerals are most common near Linden, Wis. (Fig. 2), but have also been found in some abundance at the Farrey mine at Leadmine, Wis. (Fig. 1), and uncommonly at the James mine near Shullsburg, Wis. They occur as dark-gray partial or complete replacements of millerite (Fig. 6), as coatings or overgrowths on millerite (Figs. 6 and 7), as microcrystal molds or clusters surrounding an acicular cavity that formerly held millerite (Fig. 7), and as acicular pseudomorphs after millerite crystals. Violarite and bravoite (?) commonly replace or coat only those parts of the millerite crystal not enclosed by other sulfides such as galena (Figs.

6 and 7). Violarite is identified by a diagnostic x-ray pattern, and in polished sections by a light violet-gray color, hardness ($4\frac{1}{2}$ - $5\frac{1}{2}$) and the presence of marked cleavage {001}. It is distinguished from millerite by its color, lower reflectivity, isotropism, and greater porosity (Figs. 8 and 9).

Bravoite (?) occurs sparingly in discrete grains with sharp planar boundaries (Fig. 6). It is always associated with and commonly surrounded by violarite. The bravoite (?) is distinguished from violarite in



FIG. 8. Polished section showing galena, millerite, and violarite. The large galena crystal (with triangular pits) encloses elongate blades of millerite which also extend into calcite (black) in the lower right corner. Violarite (v) which has a much lower reflectivity and is more porous than galena, replaces some of the millerite where it is not well protected from oxidation by galena. Ordinary light.

polished sections by its darker violet-gray color, its greater hardness, and lack of cleavage. It is in too small a quantity to identify with certainty.

Violarite and the associated bravoite (?) are unquestionably younger than millerite for they appear always to replace or coat acicular millerite crystals (Figs. 5, 6, 7, 8, 9, and 10). At all known occurrences of millerite near Linden (2) the nickel-iron sulfides are found in partly oxidized zinc-lead deposits, presumably in the zone of former fluctuations of the water table, suggesting that both minerals may be supergene sulfides formed by the oxidation of millerite, but not precluding their hydrothermal origin.

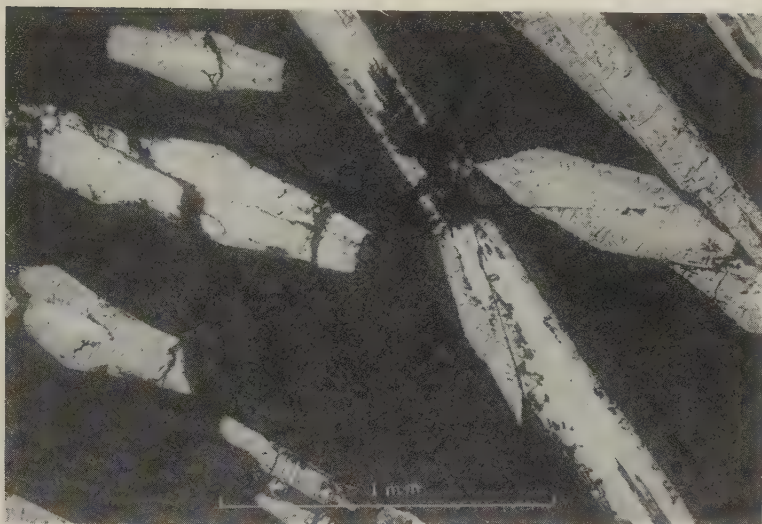


FIG. 9. Polished section showing millerite crystals (white), surrounded by violarite in calcite (very dark gray). Violarite (a little grayer than millerite) replaces the outer parts of the millerite crystals, and it is more porous and has distinct cleavage. Note the unusual twinning in the core of the six-sided millerite crystal in the right center.

Ramdohr (1955), discussing the relations of millerite and linnaeite (in which group he includes violarite), observes that linnaeite-violarite commonly is replaced by millerite as an exsolution product; whereas the opposite, replacement of millerite by linnaeite-violarite, is rare. The rela-

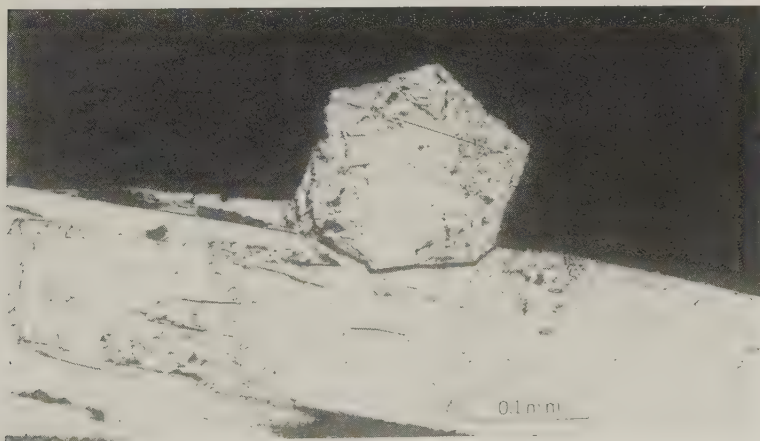


FIG. 10. Polished section showing cross and longitudinal sections of twinned millerite crystals. The twinning is brought out by natural tarnish in the laboratory.

tions described by us cannot be interpreted otherwise than as replacement of millerite by violarite.

TEMPERATURE OF DEPOSITION OF THE ORES

The temperature of deposition of the primary ore minerals of the Upper Mississippi Valley lead-zinc district has been investigated by several methods; Newhouse (1933, p. 744-750), studying liquid inclusions in sphalerite, found the temperature of deposition to be from 80° to 105°



FIG. 11. Polished section showing twinning in millerite.

C.; Garrels (1941), considering the zoning relations of sphalerite and galena, assumed concentrated chloride solutions at 100° C. under 60 atmospheres pressure; Bailey and Cameron (1951), examining liquid inclusions in calcite and sphalerite, found temperatures of formation from 75° to 121° C. Millerite presumably would be deposited at temperatures near the lower end of this range, as it is one of the last minerals deposited. Recent work by Kullerud (1953), however, based on the Zn-Fe ratio of sphalerite from the district indicates minimum temperatures of deposition for the southwestern Wisconsin deposits from less than 138° to 245° C. Field relations (Behre, Heyl, and McKnight, 1950, p. 51-69) support the lower temperatures suggested by Newhouse, Garrels, and Bailey and Cameron, rather than the higher temperatures proposed by Kullerud.

OXIDATION OF NICKEL SULFIDES

Millerite, violarite, and bravoite (?) have been altered, presumably by weathering, at many of the localities to an orange-red, yellow, or green nickel sulfate (Fig. 4) (or sulfate series). The sulfate, found only in the zone of oxidation, at (or near) the fluctuating ground water table, replaces the nickel sulfides and also forms thin crusts along cleavage planes of calcite near the original millerite clusters (Fig. 4). This sulfate is insoluble in water but is soluble with slight effervescence in dilute acid solutions; free oxygen is liberated. The movement of nickel during redeposition as secondary sulfides rarely exceeds 1 mm., but crusts of the sec-

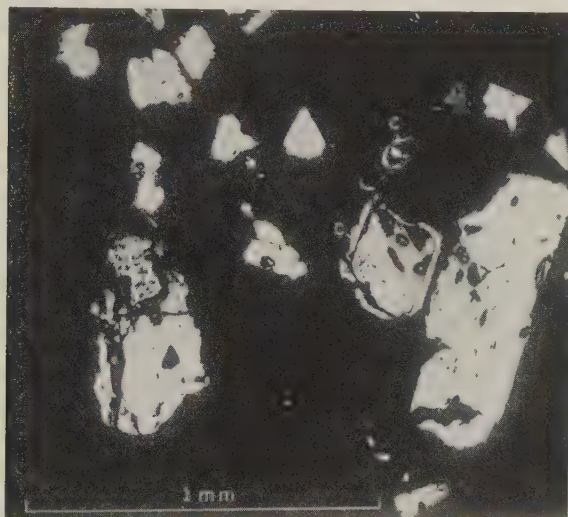


FIG. 12. Polished section showing millerite surrounded by a shell of chalcopyrite (2 grains, right center at c).

ondary sulfate mineral extend from 1 to 8 mm. beyond the original millerite crystals. Thus, nickel seems to have been more soluble in the probably acid solutions that deposited the sulfate mineral than in solutions that deposited violarite and bravoite (?).

Millerite has been found near Milwaukee, Wis. (Bagrowski, 1940, p. 556-559) and Keokuk, Iowa (Keyes, 1895, p. 401-402). Both of these localities are near but beyond the limits of the lead-zinc district. At Milwaukee, a green oxidation product of millerite called "zaratite," reported by Bagrowski (1940, p. 556-559), may be similar to one of the variations of the oxidation product at Linden.

The occurrence of a green to yellow oxidation product of millerite in Indiana has been noted by Richard C. Erd of the U. S. Geological Sur-

vey. X-ray patterns, however, are different from that of the sulfate from Linden, Wis. (Richard C. Erd, 1953, oral communication).

Howarth (1930, p. 3-5) mentions two oxidation products of millerite from a coal mine in Monmouthshire, Wales. One of these is a yellowish-green soluble nickel sulfate, probably morenosite; the second is a "sulfate insoluble in water but soluble in dilute mineral acid, presumably a basic nickel sulfate although there was insufficient material for qualitative analysis." Possibly this second oxidation product is the same as that which we call honessite.

PHYSICAL AND CHEMICAL PROPERTIES OF SECONDARY NICKEL SULFATES

The variation in color of the secondary nickel sulfate from orange to red, to yellow to green is thought to correspond to varying degrees of oxidation of the iron present. The varieties that are orange-red and yellow may be richer in ferric iron than the variety that is green. The material may actually be a series connected by $\text{FeO} \cdot \text{Fe}_2\text{O}_3$ variation as in the frondelite-rockbridgeite series, or by variations in hydrations.

Microscopic examination of the pseudomorphs after millerite shows the material to be extremely fine grained and not uniform. There is an obscurely fibrous structure, with positive elongation and extinction at about 12° . Even under high magnification very few areas are free of turbidity, and these are too small for conoscopic study. The mean index of refraction is about 1.615, and the birefringence is very low. No visible differences are apparent between the varicolored particles, except color.

In an attempt to clarify the crystalline structure of the unknown nickel sulfate, Edward Dwornik of the U. S. Geological Survey kindly prepared electron micrographs. Some of the grains suggest a stacked or layered structure similar to kaolin or mica, but the lack of indication of crystal form in the rest of the grains suggests that it is a substance of low crystallinity.

X-ray diffraction patterns from numerous samples of the material prepared by Axelrod had broad lines not referable to any known material. Besides sharp lines referable to known materials present, such as calcite, cerussite, and millerite, there were:

<i>d</i>	I	Suggested <i>hkl</i>
8.7	10	001
4.33	2	002
2.67	2	h_1k_10
1.542	2	h_2k_20

The x-ray diffraction pattern of "anodic nickel hydroxide," reported by Klug and Alexander (1954, Fig. 6-27c) is very similar to that of our material. If this material consists partly of trivalent nickel, honessite may be isomorphous with it, with trivalent iron replacing trivalent nickel.

K. J. Murata of the U. S. Geological Survey made a spectrographic analysis of the green material and found Ni, Ca, Fe, Co, and minor Pb, Mg, Mn, Si, and Zn (?).

Microchemical analyses were subsequently made on three different samples of 15 to 25 mg. in weight isolated from the same source material from Linden, Wis.

	A	B	C
NiO	42.6	33.4	35.3
CoO	3.6	3.2	1.8
FeO	2.4	N.D.	N.D.
Fe ₂ O ₃	10.5	13.7*	15.8*
CaO	2.7	10.5	2.5
SO ₃	10.8	10.7	8.6
H ₂ O—	4.7	5.1	7.1
H ₂ O+	19.7	19.5	19.7
Insol. + SiO ₂	0.9	3.4	2.2
CO ₂	absent	N.D.	N.D.
S (sulfide)	absent	absent	absent
	97.9	99.5	93.0

* Total iron calculated as Fe₂O₃.

N.D.—Not determined.

A—Robert Meyrowitz, U. S. Geological Survey, Analyst.

B, C—Charles A. Kinser, U. S. Geological Survey, Analyst; sample C was purer than sample B.

The material apparently is essentially a hydrous basic sulfate of nickel and ferric iron, and CaO is a major or minor constituent. The three analyses are by no means conclusive as to the composition of the material. Considering the nature of the material, and the small quantities analyzed (15–25 mg.), however, there is more or less agreement.

Cobalt in the secondary nickel sulfate may be derived in part from the oxidation of cobalt- and arsenic-bearing marcasite accompanying the millerite. Complex intergrowths of marcasite and a possible cobalt-arsenic mineral of somewhat similar optical properties were noted in 1946 by Milton during metallographic examinations of marcasite from the Martin mine, Benton, Wis. Spectroscopic examination suggested a mineral of the CoAsS (cobaltite), or CoAs₂ (safflorite) type. Arsenic-bearing

ores have been noted from the Linden area (Charles Singer, 1947, oral communication), where the arsenic probably occurs as this cobalt-arsenic mineral with marcasite.

The chemical literature, summarized in Mellor (1936, p. 462) lists many syntheses of basic nickel sulfates. It is not possible, however, to identify either these sulfates or the Wisconsin substance precisely enough to say that any one of them has a particular formula. Attempts to synthesize a compound having properties like those of the Wisconsin mineral were unsuccessful.

The oxidation product, thought to be a hydrated nickel-iron sulfate, and tentatively named honessite (Heyl, Milton, Axelrod, 1956) after the late Professor Arthur P. Honess of Pennsylvania State University, will require further work on better material than that available to us to define it precisely. We hope that the present admittedly unsatisfactory description will serve to bring this substance to the attention of other workers who may clarify its status as a new mineral.

ACKNOWLEDGMENTS

Although the paper is a joint effort, the first author, Heyl, is mainly responsible for the collecting of samples and descriptions of the geologic setting, paragenesis and field relations of the minerals. Milton did most of the detailed mineralogic studies and interpretations, and Axelrod is responsible for the x-ray studies.

The authors wish to acknowledge the assistance of many members of the U. S. Geological Survey in the preparation and review of the manuscript, especially R. C. Erd who also spent many hours in discussion and research on the mineralogy of these minerals. A. F. Agnew, A. E. Flint, C. E. Brown and J. W. Allingham of the U. S. Geological Survey kindly collected additional samples of the minerals for study.

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THE USE OF ZONE THEORY IN PROBLEMS OF SULFIDE MINERALOGY, PART II; THE RESISTIVITY OF CHALCOPYRITE

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ABSTRACT

Resistivity vs. temperature measurements on chalcopyrite indicate a very small activation energy for donor impurities. In a sulfur-free atmosphere dissociation occurs at a lower level of thermal energy than does intrinsic semiconductivity, suggesting a relatively large energy gap between the valence and conduction bands. Attempts to maintain equilibrium sulfur vapor pressure during resistivity measurements in order to obtain the exact band gap energy were unsuccessful. Total absence of *p*-type conductivity was noted. This implies that chalcopyrite will not occur with a cation deficiency, but will deviate from stoichiometry only with a cation excess.

INTRODUCTION

In two earlier papers (Frueh, 1954; 1955) a more or less qualitative use of zone theory was applied to several problems in sulfide mineralogy. An explanation, based on the relation between the band gap energy and the energy connected with a vacancy or interstitial impurity, was presented for the stable existence of non-stoichiometric compounds. In one example, AgCuS, it was apparent from the calculated electron-to-atom ratio necessary to fill the valence band that if this compound existed with the exact stoichiometric composition, some of the electrons would have to lie in the conduction band at a somewhat higher energy level. This might require more energy than that necessary to remove a silver atom, and, as indicated by experimental observation, the stable composition of stromeyerite would be $\text{Ag}_{1-x}\text{CuS}$, where x has some value between 0 and 0.1.

A similar explanation was advanced for the size and shape of the stability field of digenite (Cu_9S_5)-bornite (Cu_5FeS_4)-chalcopyrite (CuFeS_2). In the field from digenite to chalcopyrite the same structural type is maintained, despite the increase in the iron-to-copper ratio, by the omission of sufficient metal atoms to avoid increasing the electron-to-atom ratio beyond the capacity of the valence band.

To expand this theory and put it on a quantitative basis, a knowledge of the magnitude of the energy gap between the valence band and the conduction band is necessary. As the excess or deficiency of atoms in a non-stoichiometric compound may be treated as impurities, it would also be beneficial to have quantitative data regarding the impurity levels.

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All of this information can be secured experimentally from the measurement of the variation of electrical characteristics with temperature.

Electrical measurements have been obtained and the band structure determined for a number of semiconductors that are of interest to the electronic industry, and in a few cases, such as PbS (Scanlon, 1953; Bloem, 1956; Bloem and Kröger, 1956) and FeS₂ (Marinace, 1954; Sasaki, 1955; Otsuka, 1957), they have also been of direct interest to the mineralogist. There are many data to be obtained from naturally-occurring sulfides before optimum use can be made of existing theory. This paper contains the results of initial attempts to elucidate the band structure of chalcopyrite by this method.

Since much information on the theory and technique of the determination of band structure from the variation of electrical properties with temperature is contained in texts on semiconductors (Dunlap, 1957; Shockley, 1950) and in solid state physics texts, it will suffice here to give a brief résumé of the properties to be measured and their relation to the band structure.

At low temperatures and high purity, semiconducting materials are good insulators of electricity. They are represented in band theory (Fig. 1) as having their valence bands filled; there is a forbidden energy gap between the top of the valence band and the bottom of the conduction band. As we raise the temperature, enough energy is given to the pure semiconductor in the form of heat to lift the electrons at the top of the valence band across the energy gap to the conduction band. The material becomes a conductor because the electrons now in the conduction band are free to conduct, and because the holes left in the valence band permit a net movement of the energy states in the valence band. The latter can be looked upon as conduction by positive holes. Thus, this type of conductivity, called intrinsic semiconductivity, is made up of two types of carriers: electrons, or negative carriers; and holes, or positive carriers, that are simultaneously activated when the temperature of the sample reaches the intrinsic range.

The total conductivity is expressed mathematically by $\sigma = e(n\mu_n + p\mu_p)$, where e is the electronic charge (1.6×10^{-19} coulombs), n the number of electrons or negative carriers, p the number of holes or positive carriers, and μ_n and μ_p their respective mobilities. For intrinsic conductivity $n = p \sim \exp -\Delta E / 2kT$, where ΔE is the energy gap between the valence band and the conduction band, k the Boltzman constant, and T the absolute temperature. As resistivity is the reciprocal of conductivity, $\rho = 1/\sigma$, it follows that ΔE can be obtained from the slope of the curve $1/T$ vs. $\ln \rho$, if we assume that the change in mobilities μ_n and μ_p with temperature is small compared to the change in the number of carriers, n and p .

If we are utilizing natural samples, the possibility of obtaining very pure ones is quite remote. We must, therefore, be aware of the conductivity that arises from impurities. Also, as pointed out above, a stoichiometric excess or deficiency can be looked upon as an impurity, and therefore the activation energies of the impurity levels are a necessary and important part of the total energy picture of a non-stoichiometric compound. There are two types of impurity or extrinsic semiconductor. One is due to the presence of an impurity which, when activated, can

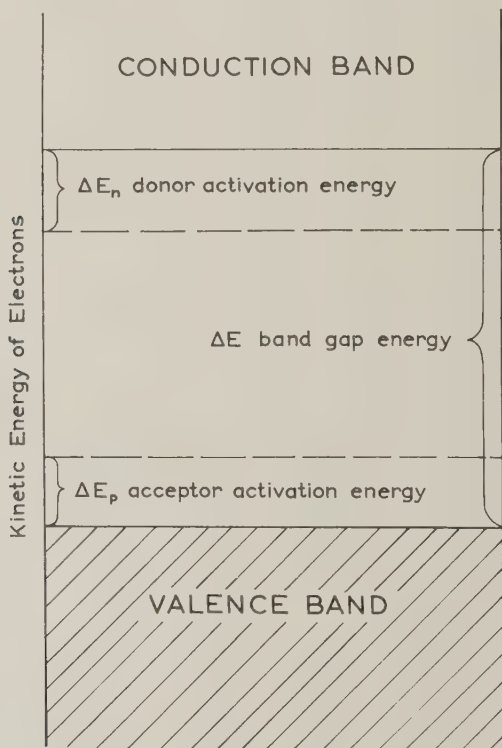


FIG. 1. Band scheme for semiconductor.

donate an extra electron to the band structure of the host semiconductor. This is called donor, or *n*-type, impurity and can be caused by an atom of a greater number of valence electrons in substitution solid solution. When activated, the extra electron would have to be accommodated in the conduction band, and thus an *n*-type semiconductor would be created. The extra electron might also be donated by the presence of a cation in interstitial solid solution, or even by a stoichiometric excess of cations.

The other type of extrinsic semiconductor is due to the presence of an impurity which, when activated, will capture or accept an electron

from the valence band, thus causing p -type, or acceptor, semiconductivity. Thus an atom substituting in a position in the structure normally occupied by one with a higher number of electrons will, when activated, act as an acceptor. The same effect can be produced by a deficiency of cations, probably resulting in vacancies (Schottky defects) which will trap electrons and cause holes in the valence band.

Two of the commonly used experimental methods for determining the type and number of carriers, and hence the kind of semiconductivity, are the determination of the Hall effect and the determination of the thermoelectric power. In the former, use is made of the fact that the holes and electrons travel in opposite directions in a sample plate during current flow. When a magnetic field is applied normal to the face of a plate, both holes and electrons will be deflected to the same side. From a measure of the sign and magnitude of the potential difference across the plate (perpendicular to both the current flow direction and the direction of the magnetic field) both the type and density of the carriers can be determined.

When a temperature difference is maintained between the ends of a specimen, an e.m.f., the thermoelectric power, is measured in millivolts/ $^{\circ}\text{C}$. by means of metal leads (usually copper) connected to the ends of the specimen. By convention, the sign of the thermoelectric effect is taken as positive if the electric current flows in the same direction as the thermal current. A positive thermoelectric sign indicates the presence of p carriers, while a negative one indicates n carriers. For most semiconductors the thermoelectric power is independent of the composition of the metal leads.

The activation energy of both types of impurity (ΔE_n or ΔE_p) can be determined by a method similar to that for determining the band gap energy: that is, from the slope of the curves in the temperature ranges where an increase in conductivity is due to the activation of only one type of carrier. Samples containing both types of impurity, in cases where both are activated over the same temperature range, are not suitable for this determination.

EXPERIMENTAL METHODS

Ideally, resistivity measurements for elucidating the band structure should be made from oriented single crystals. As there are additional energy states connected with the surfaces and interfaces of semiconductors, it is best to avoid multicrystalline samples. In an anisotropic crystal the band structure may also be anisotropic, and the energy gaps will have to be determined in different directions to get the correct picture.

Large, well-formed single crystals of chalcopyrite from French Creek, Pennsylvania; Cornwall, England; and Ugo, Japan, were used. Samples

were prepared from these crystals by slicing with a toothless band-saw blade to which #600 abrasive powder, mixed with water and glycerine, was applied. The crystal was mounted on a little dolly that was pulled forward by the weight of a few small washers on a string over a pulley, thus holding the crystal against the moving saw blade with a very light pressure. Sections were cut in various orientations, and two sample sizes, $1 \times 0.2 \times 0.1$ and $2 \times 0.5 \times 0.2$ cm., were utilized.

Resistance was measured by a null method to avoid the effect of contact resistance. A schematic diagram of the circuit used is illustrated in Fig. 2. Hall effect measurements were made by varying the slide wire potentiometer until a potential null was found, and then applying a 7000 Gauss field. All measurements were repeated after reversing the current flow through the crystal, and the results were averaged to remove any thermoelectric effect due to a possible thermal gradient in the sample.

The crystal holder, Fig. 3, was fashioned from Lavite, and gold leads were used throughout. The holder was inserted in a small furnace consisting of a vacuum bottle of Monel metal, with Kanthol windings on a ceramic core inserted in the bottle. The two-inch outside diameter of the vacuum bottle permitted it to be inserted between the poles of an electromagnet. Provision was made to introduce an inert atmosphere into the furnace.

A similar holder, for resistivity measurements alone, was constructed to fit into a silica tube, which in turn was fitted into a horizontal tubular furnace. The tube was sealed at one end, and the other end was connected to a source of H_2S for the maintenance of sulfur vapor pressure.

RESULTS

From the sign of the very small Hall effect, all the samples appeared to be *n*-type conductors at room temperature. This is in agreement with the results of other workers (Telkes, 1950) who found that, without exception, all of the twenty-two different samples of chalcopyrite measured had a negative thermoelectric effect.

Resistance measurements were made at temperatures only as low as -50° C., and from the negative slope of the $1/T$ vs. $\log \rho$ curve in this region it was evident that the *n* carriers were already activated. It can be concluded that the donor impurity level of chalcopyrite lies very close to the bottom of the conduction band, the ΔE_n being very small.

Resistance measurements were made up to 350° C. The resistance slowly increased with temperature (Fig. 4), due to the interaction of the carriers with increased thermal vibrations of the lattice, until a temperature of about 310° C. was reached. At this point the resistance reached a maximum; then, as the temperature increased, the resistance rapidly decreased, indicating a marked increase in the number of carriers.

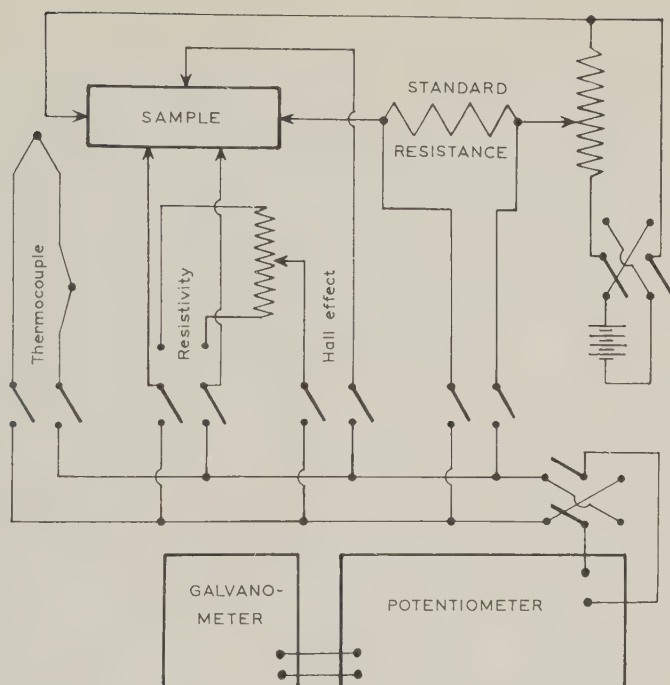


FIG. 2. Circuit diagram for Hall effect and resistivity measurements.

Upon cooling the sample, the high resistance is not recovered, but the sample returns by a lower path to a resistance considerably lower than its initial room temperature resistance. If the same sample is reheated, the curve obtained upon the previous cooling is followed until 310° , when, with increasing temperature, the resistance decreases rapidly. Again the resistance is not recovered when the sample is cooled. These runs were re-

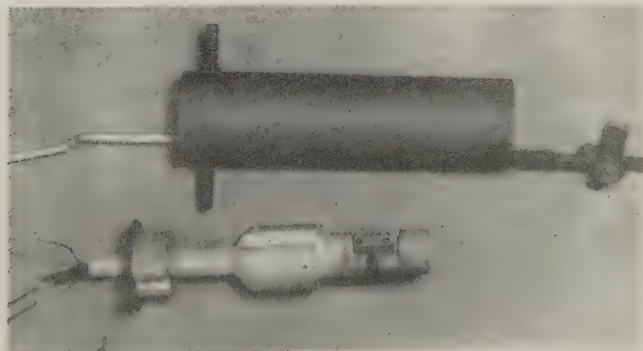


FIG. 3. Furnace and holder for Hall effect and resistivity measurements.

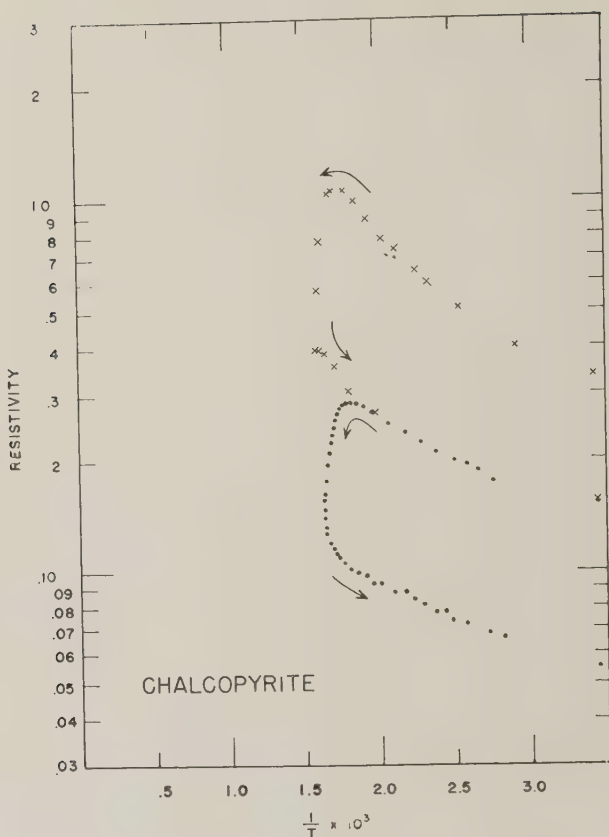


FIG. 4. Resistivity of chalcopyrite as a function of temperature in inert atmosphere. x = first run; • = second run.

peated several times with similar result until the sample became brittle and would crumble under the pressure of the electrical contacts.

It was found from a series of independent runs that the resistance curves were reproducible on heating and cooling as long as the temperature (310°) where the curve reaches its maximum resistance was not exceeded. It was also found that if a temperature higher than 310° C. is maintained for a long period of time, the resistance continues to drop, the crystal becomes brittle, and the electrical contacts are lost.

From these experiments it is evident that the creation of more electrical carriers above 310° C. is not an equilibrium process due to intrinsic semiconductivity, but rather appears to be a process in which additional carriers are caused by a deviation of stoichiometry due to partial dissociation and loss of sulfur. A similar effect was noted by Scanlon (1953) in PbS where it was found that carriers were created by dissociation

shortly after the intrinsic range was reached. Data necessary to determine the energy gap could be obtained only in the small range of temperature between where intrinsic conductivity started and dissociation took place. However, in chalcopyrite the dissociation appears to take place before the intrinsic range is reached, and therefore some means of preventing dissociation is necessary before data for the determination of the band gap energy can be obtained.

Resistance measurements were attempted in a sulfur vapor atmosphere ($\text{H}_2\text{S}-\text{H}_2$). It was soon found that too high a sulfur vapor pressure resulted in the formation of an outside coating of covellite, CuS , and the growth of pyrite, FeS_2 , within the sample. There are no data available at present on the exact sulfur vapor pressure in equilibrium with stoichiometric chalcopyrite at these temperatures.

An attempt to maintain the equilibrium vapor pressure was made by isolating a sample of chalcopyrite, to which electrical leads had been connected, in a sealed tube partially filled with finely powdered chalcopyrite. It was hoped that the fine powder about the walls of the tube would be a little warmer than the isolated sample in the middle of the tube, thus dissociating first and forming a sulfur vapor pressure that would be just enough to maintain the composition of the slightly cooler single crystal. The curve (Fig. 5) again shows lack of reversibility, and it must be assumed that the equilibrium vapor pressure is not maintained by this method.

In an investigation of the system Cu-Fe-S , Merwin and Lombard (1937) found the dissociation pressure curve for $\text{CuFeS}_{1.95}$ from 550° to 625° C. Preliminary tests were made by these investigators at temperatures from 375° to 525° C. and at sulfur pressures of 1 to 50 mm. Only above 500° C. and at pressures above 40 mm. did the results indicate systematic changes. Merwin and Lombard found that the reaction of chalcopyrite involving the absorption of sulfur lagged greatly at the lower temperatures and pressures because pyrite, one of the reaction products, was slow to crystallize, whereas loss of sulfur began without apparent lag.

They also found that samples of CuFeS_2 , heated within the range of 10 mm. to 610 mm. and from 525° to 625° C., contained small amounts of pyrite, whereas samples 0.5% by weight lower in sulfur were homogeneous. Therefore, they concluded that in this range chalcopyrite of theoretical stoichiometric composition is not quite stable.

More recently, Hiller and Probsthain (1956) found from thermal and x-ray powder studies that, when heated without a controlled sulfur pressure, the disordered phase of CuFeS_2 , stable above 550° C., slowly loses sulfur up to 720° C. when an end product poorest in sulfur is reached. This compound, which has a formula $\text{Cu}_{17+x}\text{Fe}_{17+x}\text{S}_{32-x}$ ($x \approx 0.6$), inverts

upon cooling to a cubic phase ($a=10.58$) which is still based upon face-centered close-packed sulfur atoms.

There appears to be no conflict between the results of the present research and that of earlier workers, except that the much greater sensitivity of electrical measurements allows one to detect the loss of sulfur at a much lower temperature. The loss of sulfur before the advent of the in-

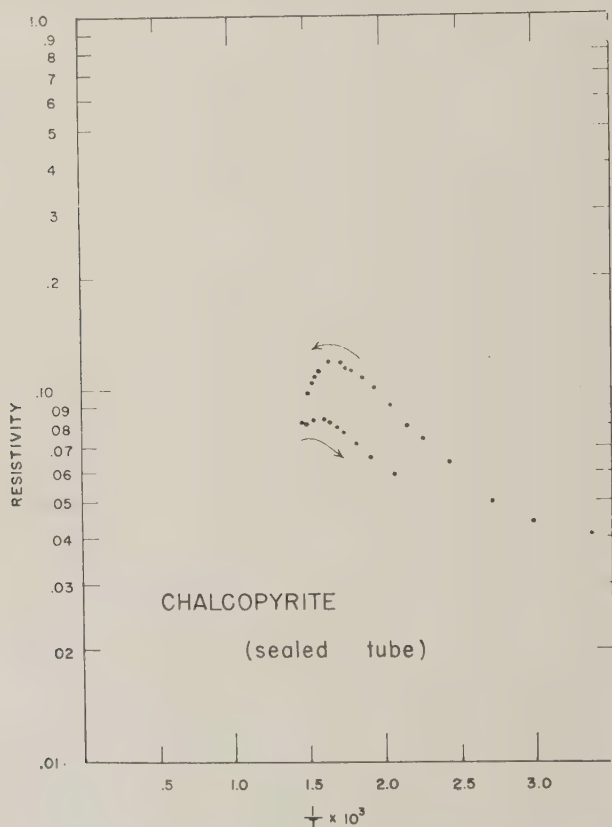


FIG. 5. Resistivity of chalcopyrite as a function of temperature in a sealed tube.

trinsic range supports the theory that the non-stoichiometric composition with extra donor atoms, in the form of a stoichiometric excess of cations, is the more stable or lower energy compound under low sulfur vapor pressure and elevated temperature conditions. This is because a relatively greater energy is required to lift the electrons across the band gap than to include and activate them in the donor level. The low activation energy of the donor-type impurities, and either the high activation energy of lack of acceptor-type impurities, as evidenced by the fact that all samples give only negative Hall and thermoelectric effects, imply that

the variation of stoichiometry in chalcopyrite will always be on the sulfur-deficient side and never cation-deficient.

Until an accurate equilibrium sulfur vapor curve for chalcopyrite from 300° C. and up is known, and resistivity is measured in a controlled atmosphere, it will be impossible to obtain the exact band gap energy by this method. However, electrical measurements (Bloem and Kröger, 1956) provide a very sensitive method for determining the vapor pressure curve. Attempts should also be made to "dope" chalcopyrite, perhaps with minute amounts of phosphorus, to see if acceptor impurities can be synthetically created and the ΔE_p determined.

ACKNOWLEDGMENTS

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AN X-RAY CRYSTALLOGRAPHIC STUDY OF
SCHROECKINGERITE AND ITS
DEHYDRATION PRODUCT

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ABSTRACT

X-ray precession patterns of schroeckingerite crystals from Moab, Utah, show that the mineral has triclinic pseudo-hexagonal symmetry. Dimensions of the unit cell containing $2(\text{NaCa}_3\text{UO}_2(\text{CO}_3)_3\text{SO}_4\text{F} \cdot 10\text{H}_2\text{O})$ are $a=9.60 \pm 0.01 \text{ \AA}$, $b=9.62 \pm 0.01 \text{ \AA}$, $c=14.46 \pm 0.01 \text{ \AA}$, $\alpha=91^\circ 42' \pm 10'$, $\beta=91^\circ 48' \pm 10'$, and $\gamma=120^\circ 05' \pm 10'$. The space group is $P\bar{1}$ or $P1$. When the material is dried at 75°C ., it loses six of the ten water molecules. The unit cell of the product has $a=b=9.52 \pm 0.02 \text{ \AA}$, $c=11.10 \pm 0.02 \text{ \AA}$, $\alpha=95 \pm 5^\circ$, $\beta=93 \pm 5^\circ$ and $\gamma=60^\circ 00' \pm 15'$, and its space group is also $P\bar{1}$ or $P1$ with $Z=2$.

INTRODUCTION

Single crystals of schroeckingerite, $\text{NaCa}_3\text{UO}_2(\text{CO}_3)_3\text{SO}_4\text{F} \cdot 10\text{H}_2\text{O}$, were examined by Hurlbut (1954), who reported that the crystals were orthorhombic, with the probable space group $Cmmm$ or Cmm . From Hurlbut's determination, it was thought these crystals would provide a relatively easy determination of the four uranium positions in the unit cell. However, the present work shows that the structure has lower symmetry.

DESCRIPTION OF THE CRYSTALS

The samples containing the single crystals of schroeckingerite were collected by Professor J. W. Gruner and the author in the summer of 1952 from the Shinarump No. 3 Mine, Seven Mile Canyon, near Moab, Utah. The specimens are from silty stringers in the Shinarump conglomerate. The rock as a whole is very porous and an ideal locality for crystal growth from evaporating aqueous solutions, which probably produced these well-formed schroeckingerite crystals. Most of the crystals grew into small cavities, attached along one edge of the pseudo-hexagonal plate. Abundant gypsum is also present.

Macroscopically, the crystals are transparent, yellow-green, pseudo-hexagonal plates which are very soft and easily bent. Their dimensions vary up to a maximum of one millimeter in diameter and 0.02 mm. thick. There is a decided tendency for one pair of opposite edges to be shorter than the others, suggesting a pseudo-orthorhombic habit rather than pseudo-hexagonal. Microscopically, most of the apparently single crystals are aggregates of several crystals and show complex extinctions in polarized light. These crystals are typified by the photograph given by Hurlbut

(1954). Several single crystals, free of secondary growths, were found which gave sharp extinctions under a polarizing microscope.

OPTICAL PROPERTIES

The optical constants for several crystals were measured, and the averages are listed in Table 1 with Hurlbut's data. The indices and pleochroism are in excellent agreement with his values, and $2V$, which was measured on a universal stage with hemispheres of index $n=1.554$, is also in reasonable agreement. The difference of 0.001 between the β index

TABLE 1. OPTICAL PROPERTIES OF SCHROECKINGERITE FROM UTAH

	This Paper	Hurlbut (1954)
α	1.491	1.490
β	1.537	1.537
γ	1.538	1.538
$2V$	22.5°	18°
Optic sign	(—)	(—)
Pleochroism		
X	very pale yellow	very pale yellow
Y	yellow-green	yellow-green
Z	yellow-green	yellow-green

and γ index, which Hurlbut emphasized, was noted in the present study. During the determination of $2V$ it was observed that the acute bisectrix, which should be normal to the plane of the plate if the crystal is orthorhombic, deviated from the normal by approximately one degree. This departure may be within experimental error and, therefore, is not strong enough evidence to eliminate the possibility of classifying the crystal as orthorhombic. The optical orientation noted is X perpendicular to the plate, Y in the plane of the plate perpendicular to the short edge, and Z parallel to the short edge, which corresponds with Hurlbut's orientation: $X=c_0$, $Y=b_0$, and $Z=a_0$.

UNIT CELL AND SPACE GROUP

Precession patterns about the c -axis and two axes nearly at 90° to the c -axis were obtained from two single crystals using molybdenum $K\alpha$ ($\lambda=0.7107\text{\AA}$) and $\mu=30^\circ$. One crystal was oriented with the rotation axis normal to the plane $\bar{1}10$ and essentially parallel to Y, and very clear $hk0$, $hk1$, $hk2$, $hk3$, $hk4$, and $\bar{h}hl$ (Hurlbut's $0kl$) zones were obtained. The other was mounted at a corner of the plate with the rotation axis normal to the plane $\bar{2}10$, and patterns of $hk0$ and $2\bar{h}$, h , l (Hurlbut's h ,

$3\bar{h}, l$) were made. Minor differences in relative intensities were observed when the $hk0$ patterns of the two crystals were compared, but the over-all features were almost identical. Both $hk0$ zones and the $\bar{h}hl$ and $2\bar{h}, h, l$ zones showed the required center of symmetry; the upper level patterns showed no symmetry at all.

If the crystal were orthorhombic, the optical orientation would require one crystallographic axis normal to the plane of the plate and the other two in the plane. Because mm symmetry is not observed in the $hk0$ zones, the orthorhombic possibility is ruled out. If the crystal were monoclinic, the optical orientation would require the unique axis to lie either parallel to X, which is normal to the plate, or parallel to Y or Z in the plane of the

TABLE 2. PSEUDO-ORTHORHOMBIC CELL OF SCHROECKINGERITE

	This Paper	Hurlbut (1954)
a_0	9.59 Å	9.69 Å
b_0	16.69 Å	16.83 Å
c_0	14.46 Å	14.26 Å
α_0	89°15'	90°
β_0	93°50'	90°
γ_0	89°55'	90°
Volume	2,308 Å ³	2,322 Å ³

plate. The latter possibilities (unique axis equal Y or Z) would require the $hk0$ zone to have mm symmetry and all upper levels along the c -axis to have m symmetry; while the former orientation (unique axis equals X) would require 2 symmetry of all these zones and mm symmetry of $\bar{h}hl$ and $2\bar{h}, h, l$. Because neither set of conditions is present, the crystal must be triclinic with the space group either $P\bar{1}$ or $P1$. The morphology strongly indicates $P\bar{1}$.

The cell most nearly corresponding to Hurlbut's orthorhombic cell is given in Table 2, and his values are also listed for comparison. Using four formula units with a formula weight of 888.56, the calculated specific gravity is 2.550, which compares well with the value of 2.544 given by Hurlbut. For triclinic symmetry this cell is twice as large as necessary, and only two formula units are in the unit cell. Because triclinic symmetry does not specify a unique set of axes, a cell was chosen to correspond to the Delaunay (1933) reduced cell. This triclinic cell is related to the pseudo-orthorhombic cell by the reciprocal lattice relations $a^* = a_0^* - b_0^*$, $b^* = a_0^* + b_0^*$, and $c^* = c_0^*$, where the subscript $(_0)$ indicates

the orthorhombic parameters. The resulting cell dimensions are as follows:

$$\begin{array}{ll} a = 9.60 \pm 0.01 \text{ \AA} & \alpha = 91^\circ 42' \pm 10' \\ b = 9.62 \pm 0.01 \text{ \AA} & \beta = 91^\circ 48' \pm 10' \\ c = 14.46 \pm 0.01 \text{ \AA} & \gamma = 120^\circ 05' \pm 10' \\ \text{Volume} = 1154 \text{ \AA}^3 \end{array}$$

The cell is very nearly hexagonal, having a γ angle of 120° within the limits of error, and an axial ratio of $a:b:c = 0.9979:1:1.5031$. The matrix transforming Miller indices given by Hurlbut to correspond with this cell is

$$\begin{bmatrix} 1/2 & 1/2 & 0 \\ -1/2 & 1/2 & 0 \\ 0 & 0 & 1 \end{bmatrix}.$$

CONCLUSIONS

In view of the optical evidence, the very close agreement in orthorhombic cell parameters, and the fact that they are from the same source, the crystals used for this study are believed to be identical with the ones used by Hurlbut. Possibly twinning could explain the orthorhombic symmetry which he reported, although none was noted in this study. The variation in relative intensities noted in the $hk0$ zones of the two crystals, used in this study, may be due to a difference in water content which was shown by Hurlbut to affect the optical constants of a schroeckingerite from Argentina.

THE DEHYDRATION PRODUCT

Several good crystals of schroeckingerite were dried in an oven at 75°C . for about 4 hours and then placed in a desiccator over anhydrous CaSO_4 . The crystals were cloudy and appeared to be somewhat porous. The (001) face was pitted, and under the petrographic microscope the crystals lying on this face showed undulatory extinctions. The optical properties of the dehydrated material are given in Table 3. The difference in the α indices may be experimental error because of the difficulty of standing a thin plate on edge in immersion oils and the cloudiness of the crystals. As nearly as could be determined on the imperfect crystals, the optic axis is normal to the plane of the plates. A slight separation of the isogyres, indicating a maximum $2V$ of 5° , was observed during rotation of the nearly uniaxial interference figure. This separation could be caused by distortions in the crystals and therefore is not definitely established.

TABLE 3. OPTICAL CONSTANTS FOR DEHYDRATED SCHROECKINGERITE

	This Paper	Hurlbut (1954)
α	1.518	1.532
β	1.582	1.582
γ	1.582	1.582
Sign	(-)	(-)
2V	0°-5°	0°
pleochroism		
X	pale yellow	colorless
Y	yellow-green	pale yellow
Z	yellow-green	pale yellow

X-Ray Data

The optical data indicate that only zones parallel or normal to the $hk0$ zone need be examined to reveal the symmetry relationships. Precession patterns using molybdenum $K\alpha$ radiation and $\mu=30^\circ$ were obtained of the $hk0$, $hk1$, and $0kl$ zones from one crystal. The $hk0$ pattern was very clear and lattice parameters could be measured with some accuracy. The $hk1$ zone was nearly as sharp, but some streaking of the spots due to warping of the crystal was evident. The $hk0$ zone showed 6-fold symmetry, but the $hk1$ zone showed no symmetry. The $0kl$ pattern showed sharp reflections only along $00l$, and very diffuse reflections smeared out parallel to $00l$ were noted for values of k up to 9. When this $0kl$ pattern is examined closely, the k -streaks reveal intensity variations giving the pattern only the required center of symmetry. Using the same reasoning as for schroeckingerite on the relationships between optical data and x-ray data, the symmetry for these crystals can be no higher than triclinic. The unit cell is very nearly hexagonal, differing only in the departure of the c -axis by a few degrees from normal to the ab -plane. Because of the poor $0kl$ pattern it was impossible to determine the departure accurately, and

TABLE 4. CELL CONSTANTS FOR DEHYDRATED SCHROECKINGERITE

	This Paper	Hurlbut (1954)
a	$9.52 \pm 0.02 \text{ \AA}$	$9.72 \text{ \AA}$
b	$9.52 \pm 0.02 \text{ \AA}$	$9.72 \text{ \AA}$
c	$11.10 \pm 0.02 \text{ \AA}$	$11.03 \text{ \AA}$
α	$95^\circ \pm 5^\circ$	90°
β	$93^\circ \pm 5^\circ$	90°
γ	$60^\circ 00' \pm 15'$	60°
Volume	$870 \text{ \AA}^3$	$902 \text{ \AA}^3$

only estimated angles can be given for α and β . The cell constants are given in Table 4, with Hurlbut's values for comparison.

Using the measured specific gravity of 2.86 and the formula $\text{NaCa}_3\text{UO}_2(\text{CO}_3)_3\text{SO}_4\text{F} \cdot 4\text{H}_2\text{O}$ for the dehydrated material as established by Novacek (1939) and verified by Hurlbut, one finds 1.92 formula weights per unit cell. The difference from 2.00 may be due to the formation of open cavities on dehydration as evidenced by the cloudy appearance of the crystals.

CONCLUSIONS

When x-ray diffraction patterns of the dehydrated material are compared with the corresponding zones of schroeckingerite, there are actually only small differences in relative intensities, indicating that the main features of the structure are retained on dehydration. The hexagonal symmetry of the $hk0$ photograph of the dehydrate indicates that the projection of the structure along the c -axis must have approximately hexagonal or trigonal symmetry even though the whole structure does not possess this symmetry. That the structure is not hexagonal as originally proposed is strongly suggested by the large number of atoms in special positions which would be required to accommodate only two formulas per unit cell of the dehydrated material. Careful measurements of the $hk0$ intensities may show departures from hexagonal symmetry in that zone also.

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SCHUETTEITE, A NEW SUPERGENE MERCURY MINERAL*

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ABSTRACT

Basic mercuric sulfate, $\text{HgSO}_4 \cdot 2\text{HgO}$, has been found as a supergene mercury mineral in several quicksilver deposits in the more arid parts of the western United States, and is a common product on dumps of burnt ore and bricks from old mercury furnaces. This new mineral is named schuetteite after Curt Nicolaus Schuette, mining engineer, geologist, and specialist on mercury deposits.

As schuetteite has been found in natural occurrences only as thin films, it has been identified by comparing its x -ray pattern with that of basic mercuric sulfate prepared in the laboratory. Crystal, chemical, and microscopic data have been obtained chiefly from similar material occurring in greater abundance in dumps and old furnace bricks.

Schuetteite is canary yellow in color, but it differs from the yellow mercury oxychlorides in that it does not darken on exposure of bright light. No crystals suitable for goniometric or precession camera work have been found, but minute tabular hexagonal crystals lying in a flat position were observed to be dark between crossed nicols. The writers, knowing the mineral was hexagonal, indexed the x -ray powder patterns by using a simple and direct method, which appears not to be in general use, involving the known chemical formula and density. The hexagonal mineral has a cell with $a=7.07$ Å, $c=10.9$ Å (both ± 0.01 Å) and a calculated density of 8.36 gm/cm^3 . The observed specific gravity is 8.18.

Optically schuetteite is uniaxial, negative. Both indices of refraction are well above 2.10; birefringence is moderate to high. It is slightly pleochroic with $E=\text{orange-yellow}$ and $O=\text{greenish-yellow}$.

In natural occurrences schuetteite has been found on cinnabar surfaces exposed to sunlight. It is believed to have formed through direct oxidation of cinnabar by oxygen-bearing surface water with sunlight providing energy to cause the reaction. HgSO_4 may be an intermediate product.

On dumps of burnt ore and on furnace bricks the basic mercuric sulfate forms beneath the surface and a different reaction is required. In these places it appears to result from the action of strongly acid sulfate waters on metallic mercury. This reaction requires higher acidity and more strongly oxidizing conditions than are normally met in nature; in those natural environments where such conditions might occur, mercury generally is present as a sulfide rather than as the native element. It therefore seems unlikely that quicksilver deposits have anywhere been appreciably leached or enriched by either of the processes that lead to the formation of the basic mercuric sulfate.

INTRODUCTION

Schuetteite, a new mineral with the composition of basic mercuric sulfate, $\text{HgSO}_4 \cdot 2\text{HgO}$, has been found in small amounts in natural occurrences in several quicksilver deposits in Nevada, and in single localities in California, Oregon, and Idaho. The same material occurs in abundance on bricks of old Scott-type quicksilver furnaces and on dumps of furnaced ore in many other places. Its identity in natural occurrences has been

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established by comparing its x-ray pattern with the pattern of basic mercuric sulfate prepared in the laboratory.

It seems fitting that this new mercury mineral, which is the first to be discovered¹ since 1910 (Canfield, Hillebrand, and Schaller, 1910), be named for Curt Nicolaus Schuette (pronounced shōō' tê), mining engineer and geologist, who has devoted much of his life to the study of mercury deposits. He has written reports on quicksilver mining and economics (Schuette, 1931*a*), on the metallurgy of quicksilver (Duschak and Schuette, 1918; Schuette, 1931*b*, 1931*c*), the geology of quicksilver deposits of Oregon (Schuette, 1938) and of the world (Schuette, 1930). He also has successfully operated several of the largest quicksilver mines in the United States.

PHYSICAL PROPERTIES

The color of schuetteite is canary yellow, which along with its association with other mercury minerals permits its ready recognition in the field. Specimens exhibit a range in color from greenish-yellow through a shade that exactly matches the color of most carnotite to a somewhat orangey-yellow in the coarsest crystals found in old furnace bricks. Its color may in places resemble the color of the mercury oxychlorides, eglestonite and terlinguaite, but both of these darken rapidly on exposure to sunlight whereas the yellow color of schuetteite remains unchanged.

The hardness appears to be about 3 on Mohs' scale, as determined by dragging minute grains of schuetteite, under a glass slide, across the surface of gypsum and calcite cleavage plates. However, as the mercury mineral is quite friable and readily reduced to dust, this test may not have yielded accurate results.

The specific gravity is 8.18, determined by using a 5 ml. fused silica Adams-Johnston pycnometer and applying a vacuum to remove air from a finely ground sample of synthetic schuetteite. The calculated density is 8.36 gm./cm.³, based on composition and size of the unit cell.

OPTICAL PROPERTIES

Schuetteite is uniaxial, negative. Basal hexagonal plates observed under the oil immersion lens are sensibly dark between crossed nicols, but are much too small to yield an interference figure. Both indices of refraction are well above 2.10; the birefringence is moderate to high. All sections are yellow; however, crystals are slightly pleochroic with E = orange yellow and O = greenish yellow.

¹ The name moschellandsbergite was introduced in 1938 by Berman and Harcourt (1938) for amalgam with a composition of Ag₂Hg₂; however, this is regarded as a redefinition of previously known material rather than a new discovery.

CRYSTALLOGRAPHY

Microscopic examination and x-ray diffraction studies reveal that schuetteite is hexagonal, but no crystals suitable for goniometric or precession camera work have been found. Natural occurrences of the mineral consist of thin earthy films, in many places accompanied by opal. Although the material found on bricks of demolished furnaces generally is sufficiently crystalline to exhibit a sparkle from minute crystal faces, the crystals are so clustered as to prove unsuitable for determination of the crystal morphology. Material from the dump of the Oceanic mine contained some minute crystals that were thin hexagonal plates and others that had a small hexagonal prism and steep hexagonal dipyramidal (?) faces. To confirm the apparent hexagonal character of schuetteite an attempt was made by Marie Lindberg, of the U. S. Geological Survey, to prepare electron diffraction patterns from the basal plates. However, no pattern could be obtained, probably because the thin plates were quickly volatilized by the electron beam.

X-RAY DATA

As the habit and uniaxial character of schuetteite suggested that the mineral was hexagonal, an attempt was made to index the x-ray powder pattern, assuming hexagonal symmetry. This attempt was entirely successful.

The initial derivation of the values of a and c of the hexagonal cell from the observed powder pattern data was made in a direct and simple way, using the known chemical formula and density. The volume of a hexagonal cell, $V(\text{\AA}^3)$, is related to the density, $\rho(\text{gm./cm.}^3)$, the formula-weight of the compound, F.W. (gm.), the number of formula-weights per unit-cell, Z , and the interplanar spacings $d_{10.0}$ and $d_{00.1}$ (both in $\text{\AA}$), by the following expression:

$$V = (2/3^{1/2})d_{10.0}^2 d_{00.1} = \frac{Z \times (\text{F.W.})}{6.023 \times 10^{23} \times \rho \times 10^{-24}} \quad (1)$$

For schuetteite, F. W. = 729.90, and $\rho = 8.18$ (taking the density equal to the observed specific gravity). Substituting these values into (1), we obtain:

$$d_{10.0} = (11.328 Z^{1/2})/d_{00.1}^{1/2} \quad (2)$$

or

$$hd_{h0.0} = (11.328 Z^{1/2})/(ld_{00.1})^{1/2} \quad (3)$$

Several values of the observed d -spacings from Table 1 were tentatively assumed to represent $d_{00.1}$, and values for $d_{10.0}$ were calculated from (3), for several values of Z . By the use of this method it very soon became ap-

parent that the observed values of 6.13 Å and 3.35 Å, of Table 1, represent $d_{10.0}$ and $d_{00.3}$, respectively, and that $Z=3$. From a consideration of a large number of the observed spacings, the unit-cell constants that best fit all the data were selected as $a=7.07_0$ Å and $c=10.0_5$ Å (both ± 0.01 Å). All possible $d_{hk.l}$ were calculated on the basis of these unit-cell constants, using the expression

$$\frac{1}{d_{hk.l}} = \left[\frac{4}{3a^2}(h^2 + hk + k^2) + \frac{l^2}{c^2} \right]^{1/2};$$

the calculated spacings are listed in Table 1. The calculated density is 8.36 gm./cm.³, which compares favorably with the measured specific gravity of 8.18. It will be noted from Table 1 that there are no systematic extinctions leading to a rhombohedral cell. In addition it will be noted that with the exception of the very weak line of spacing 9.5 to 9.6 Å, all the observed reflections of the type 00. l obey the criterion $l=3n$ only.

The line of spacing 9.5 Å occurs on powder pattern photographs made with Cu/Ni radiation just at the edge of the region of heavy scattering around the central beam, and consequently it is difficult to measure it accurately, or even to decide whether it is, in fact, present in some of the films studied. Attempts made to record the line on diffractometer tracings and on powder pattern photographs using Cr/V radiation were unsuccessful.

If it is assumed that the line is due to a constant impurity such as some decomposition product of $\text{HgSO}_4 \cdot 2\text{HgO}$, then the criterion holds that for 00. l reflections $l=3n$ only and that schuetteite contains a 3₁, 3₂, 6₂, or 6₄ axis and has one of the ten space groups compatible with these screw axes listed in International Tables (1952). If, on the other hand, the 9.5 Å line is truly the 00.1 line, then schuetteite has a pseudo screw axis of the kind listed above. Such a pseudo screw axis would be due to the arrangement of the relatively heavy mercury atoms.

Although the method expressed by (3) above is perfectly general, where the chemical formula and density are known and the symmetry is suspected, and is quite easy to apply in practice, it does not seem to be in common use.

CHEMICAL PROPERTIES

The assignment of the chemical formula of $\text{HgSO}_4 \cdot 2\text{HgO}$ to schuetteite is based on the identity of its x-ray pattern with that of the artificial compound, which can be readily prepared by adding water to solid mercuric sulfate after the equation:



TABLE 1. X-RAY DATA FOR SCHUETTEITE— $\text{HgSO}_4 \cdot 2\text{HgO}$
HEXAGONAL; $a = 7.07_0 \text{ \AA}$, $c = 10.0_5 \text{ \AA}$ (BOTH $\pm 0.01 \text{ \AA}$)

Measured*					Calculated†	
Cu/Ni		$\lambda K\alpha = 1.5418 \text{ \AA}$ $\lambda K\alpha_1 = 1.5405$ $\lambda K\alpha_2 = 1.5443$				
I/I_0^{**}	$d_{hk.l}^1$	$d_{hk.l}^2$	$d_{hk.l}^3$	$d_{hk.l}^4$	$d_{hk.l}$	$hk.l$
<5 ⁵		9.5	9.6	9.5	10.0	00.1
11	6.13	6.11	6.11	6.11	6.12	10.0
22	5.22	5.19	5.19	5.21	5.21	10.1
					5.02	00.2
4	3.87	3.85			3.88	10.2
					3.54	11.0
69	3.35	3.34	3.34	3.34	3.35	00.3
<5		3.33			3.34	11.1
5	3.06	3.04		3.04	3.06	20.0
100	2.92	2.91	2.91	2.92	2.94	10.3
					2.93	20.1
					2.89	11.2
55	2.61	2.60	2.60	2.61	2.61	20.2
					2.513	00.4
3	2.43	2.42			2.432	11.3
<5		2.32		2.32	2.324	10.4
15	2.315	2.30		2.30	2.314	21.0
					2.260	20.3
7	2.25	2.24	2.24	2.25	2.255	21.1
2	2.10	2.09		2.09	2.102	21.2
		2.040			2.048	11.4
					2.041	30.0
					2.010	00.5
3	1.99	1.989		1.989	2.000	30.1
26	1.937	1.933	1.933	1.937	1.942	20.4
<5		1.899	1.899	1.888	1.910	10.5
6	1.900				1.904	21.3
3	1.887	1.881			1.891	30.2
16	1.763	1.762	1.762	1.762	1.768	22.0
<5		1.755		1.755	1.747	11.5
6	1.741	1.737	1.737	1.737	1.743	30.3
6	1.739	1.731		1.731	1.741	22.1
					1.702	21.4
5	1.696	1.695		1.695	1.698	31.0
15	1.674 ⁶	{1.675 1.670}	1.675	{1.675 1.667}	1.680	20.5
					1.675	00.6

* The powder patterns made photographically were taken with Debye-Scherrer powder cameras of 114.59 mm. diameter, using the Straumanis technique. The lower cut-off limit is at 2θ of approximately 7° ($13 \text{ \AA}$).

** Intensities from diffractometer tracing except those marked <5 or <3.

† Spacings calculated for $d \geq 1.5 \text{ \AA}$ only.

¹ $\text{HgSO}_4 \cdot 2\text{HgO}$ from burnt ore dump, Oceanic mine, San Luis Obispo Co., Calif. Diffractometer tracings run between $2\theta = 4^\circ$ and $2\theta = 106^\circ$. Error in peak-position measurement approximately $\pm 0.1^\circ$ (2θ).

² Synthetic schuetteite prepared by treating HgSO_4 with H_2O , washing and decanting excess H_2SO_4 . This product was used for the chemical analysis. Film No. 7532.

³ Schuetteite furnace deposit from the Chisos Furnace, Terlingua district, Trans Pecos, Texas. Film No. 6362.

⁴ Schuetteite from the B. and B. mine, Nevada. Film No. 6355.

⁵ Intensities marked <5, or <3 are estimated from powder films.

⁶ Doublet.

TABLE 1 (continued)

		Measured*			Calculated†	
Cu/Ni		$\lambda K\alpha = 1.5418 \text{ \AA}$ $\lambda K\alpha_1 = 1.5405$ $\lambda K\alpha_2 = 1.5443$				
<5 3	1.610	1.610 <i>b</i> ⁷		1.608 <i>b</i>	1.674	31.1
					1.667	22.2
					{1.616	10.6
					{1.609	31.2
18 3	1.558 1.528	1.556 1.526	1.558	1.556 1.523	1.584	30.4
					1.563	22.3
					1.531	40.0
					1.518	21.5
10 <5 7 2 2 4 5 2 3 5 5 7 2 1	1.510	1.508 1.488 1.459 1.441	1.508	1.508 1.441 1.427 1.400	1.515	31.3
					1.514	11.6
					1.513	40.1
2 2 4 5 2 3 5 7 2 1	1.461 1.443 1.430 1.404	1.459 1.441 1.427 1.399	1.459	1.441 1.427 1.400 1.388		
2 3 5 5 7 2 1	1.389 1.352 1.324 1.305	1.388 1.352 1.321 1.302	1.388	1.388 1.352 1.323 1.302		
2 3 5 5 7 2 1	1.297 1.213 1.188 1.181	1.296 1.213 <i>b</i> 1.188 1.180 <i>b</i>	1.296	1.298 1.215 <i>b</i> 1.163 1.144 α_1		
<5 6 4 6 4 2 1	1.159 1.147 1.144 1.125	1.158 1.144 α_1 1.145 α_2 1.123 α_1	1.158	1.163 1.144 α_1 1.123 α_1 1.123 α_1		
4 2 1 2 1 3 2 2 2 3 2	1.122 1.111 1.102 1.092	1.124 α_2 1.110 1.094 α_1 1.091 α_2	1.124 α_1	1.110 1.094 α_1 1.071 <i>b</i> 1.048 α_1		
1 3 2 2 2 3 2 2 2 3 2	1.073 1.049 1.045 1.013	1.072 <i>b</i> 1.047 α_1 1.045 α_2 1.017	1.047 α_1	1.071 <i>b</i> 1.048 α_1 1.017 1.017		
<3 3 2	1.000 0.974	1.001 α_1 1.001 α_1 .999 α_2 .974 <i>b</i>	1.001 α_1	1.001 α_1 1.001 α_1 .999 α_2 .960 <i>b</i>		
2	0.974	.951 <i>b</i> .942 <i>b</i> .929 <i>b</i> .914 <i>b</i>		.898 <i>b</i>		

⁷ *b* = broad.

To verify the identity of the synthetic material an analysis was made which yielded 88.9 per cent HgO and 11.3 per cent SO₃, which agrees closely with a theoretical 89.0 and 11.0 per cent for the basic mercuric sulfate.

Material from the Oceanic mine dump, which gives an identical powder pattern, was purified for analysis insofar as possible by fine grinding, repeated centrifuging, and flotation. Its analysis is shown in Table 2. The sample proved to be only a little more than 80 per cent pure, with the

TABLE 2

Analysis		Recalculated to include only HgO and SO ₃	Theoretical HgSO ₄ · 2HgO
HgO ¹	71.44	87.7	89.0
SiO ₂	12.74		
Fe ₂ O ₃	1.22		
TiO ₂	0.20		
Al ₂ O ₃	0.54		
CaO	0.08		
MgO	0.06		
SO ₃	9.99	12.3	11.0
H ₂ O*	3.73		
	100.00	100.0	100.0

¹ Weighed as metal after amalgamation with a preweighed gold bar (Fahey, 1937).

* By difference.

chief impurities being opal, hematite, and cinnabar. The small amount of cinnabar caused a lowering of the mercury-sulfur ratio. Spectroscopic analysis of the same sample did not reveal other elements to be present in quantities larger than 0.01 per cent.

OCCURRENCE

Schuetteite has been found as a naturally occurring supergene mineral in six quicksilver mine areas in Nevada, and at single mines in Oregon, Idaho, and California (see Fig. 1). In all of these places it occurs as thin films on surfaces of cinnabar-bearing rocks that are exposed to sunlight. It does not penetrate the rocks except to depths of less than 1 mm. along cracks, and none has been found in the numerous underground workings in these mine areas.

All but one of the Nevada occurrences, and the Idaho and Oregon localities, are at quicksilver deposits of the opalite type (Bailey and Phoenix, 1944, p. 17-21). In these deposits cinnabar generally occurs in a

widespread blanket of rock known as opalite, formed by the leaching and silicification of acid tuffs or siliceous sediments. The opalite is cryptocrystalline, and the widely used name is a misnomer as chalcedonic quartz, rather than opal, is generally the predominant mineral. The cinnabar occurs as clouds of disseminated crystals, generally of minute size (Pollock, 1944, p. 2), in favorable layers or along feeder faults. Calomel, mercury oxychlorides, and native mercury have been found at the Opalite mine in Oregon and elsewhere, but they are not common in this

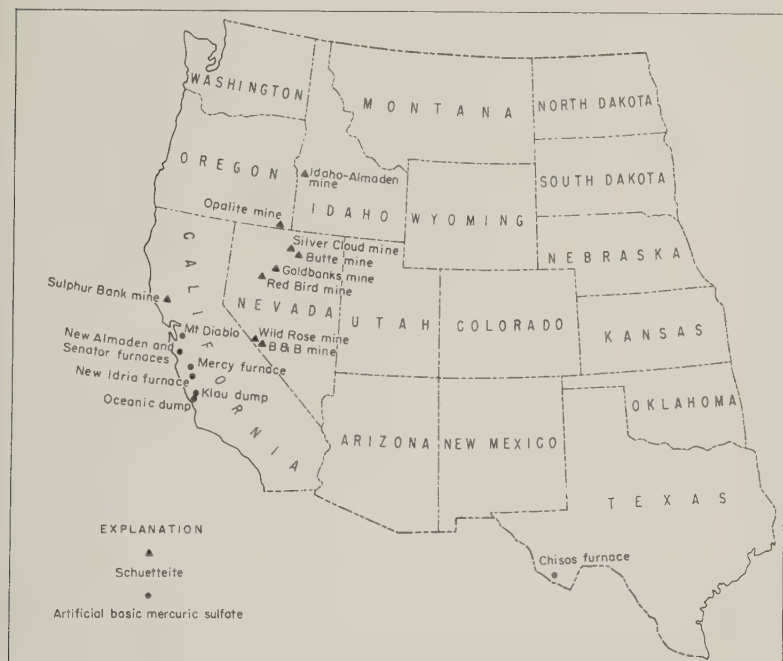


FIG. 1. Index map showing localities where schuetteite has been found, and showing other occurrences of basic mercuric sulfate.

type of deposit. Other minerals, except for relict quartz, are generally rare or absent. Some opalite deposits contain alunite, and a few of the rocks found coated with schuetteite contain a little of this mineral. Except for cinnabar, pyrite is the only other sulfur-bearing mineral occurring in opalite deposits, and it is so rare that it has been observed only as a few minute crystals in a single deposit.

Schuetteite is most easily found at the Silver Cloud mine in the Ivanhoe district about 30 miles north of Battle Mountain, Nevada (Bailey and Phoenix, 1944, p. 61-63). Here an open cut has been stripped to the

undulating surface of a particularly hard layer of opalite that only locally contains concentrations of cinnabar. Schuetteite is scattered over this surface, forming nebulous blooms almost a foot in diameter in places where there is also a concentration of cinnabar. The cinnabar has turned black from exposure to sunlight, forming a background on which the thin films of bright yellow schuetteite are readily seen. The open cut was developed to its present depth shortly before the mine was visited by Bailey in 1943; the schuetteite formed between that date and 1956 when it was revisited.

The mineral is also readily found at the B. and B. mine on the east slope of the White Mountains, Esmeralda County, Nevada (Bailey and Phoenix, 1944, p. 67-70). It is most abundant on the steep wall forming the northeastern part of the main glory hole that has been excavated in flat beds of sintery opalite. The glory hole was developed between 1927 and 1930. When Bailey mapped the deposit in 1941 only a little schuetteite was noted in the area, but by 1956 considerable quantities of the mineral had formed. In 1941 it was also collected from loose opalite blocks in the floor of a second pit below the furnace site. Here alunite is present in some of the opalite, and hyaline opal is closely associated with the schuetteite.

Other opalite deposits where schuetteite has been found are the Wild Rose mine, the Velvet working of the Butte mine, and the Goldbanks mine in Nevada (Bailey and Phoenix, 1944, p. 74-75, 56-68, and 170-171), the Opalite mine in southeastern Oregon (Yates, 1942, p. 343-344), and the Idaho-Almaden mine east of Weiser, Idaho (Ross, 1956, p. 95-99).

At the Red Bird mine east of Lovelock, Nevada (Bailey and Phoenix, 1944, p. 167-168) schuetteite was found on a single specimen of rich ore on the waste dump. It selectively coats crystals of cinnabar up to 3 mm. in diameter occurring in a gangue of limestone and quartz.

At the famous Sulphur Bank mine in Lake County, California (Everhart, 1946) thin films of what is probably schuetteite were found on cinnabar-bearing leached basalt between the Northwest Pit and the Basalt Pit. Because of the scarcity of material its identity has not been verified by x-rays. This is an area of continuing hydrothermal activity where the surface waters are highly acid. The environment is comparable to that which prevails in some of the artificial occurrences discussed in the following paragraphs.

Basic mercuric sulfate has also been found in many places where it cannot properly be considered a naturally occurring mineral. Some description of these occurrences seems warranted because the sulfate was apparently formed through a different process than that responsible for

most of the natural occurrences. These places include bricks from old Scott-type furnaces formerly widely used for treating quicksilver ore, and dumps of furnaced rock, generally called calcine.

Clots of crystals of macroscopic size form coatings several millimeters thick on the bricks of the dismantled Chisos mine furnace in Brewster Co., Texas. Similar material has been noted in California at the New Almaden and Senator mines in Santa Clara County, the Mercy mine in Fresno County, and the Sulphur Bank mine in Lake County, Mercury sulfate was also referred to as coating the condensers at the Corona mine and the furnaces of the Sulphur Bank and New Idria mines (Bradley, 1918, p. 81, 236). In these occurrences it is in some places closely associated with artificial gypsum, calomel, montroydite, and cinnabar, but metallic mercury, which occurs as droplets in many old furnace bricks, has not been seen with the mercuric sulfate. In contrast to the naturally occurring surface films, the artificial material not only encrusts the bricks but also occurs in pores within them where no sunlight could have penetrated.

The basic mercuric sulfate has been found on calcine dumps in several localities, the most notable of which is at the Oceanic mine in San Luis Obispo County, California. In a part of this dump of burnt ore the sulfate occurs as minute crystals and earthy bunches in a layer of fine-grained debris extending from the surface to a depth of at least $1\frac{1}{2}$ feet. The yellow sulfate amounts to more than 10 per cent of the material in part of the dump, and it constitutes good retort ore containing hundreds, if not thousands, of dollars worth of mercury. The material has been left behind by retort operators, as have the yellow coated bricks in other places, because it is not red like cinnabar and contains no visible mercury. The "gangue" here consists of opal, much of which is attached to the mercuric sulfate, gypsum, cinnabar, iron oxides, quartz, and rock fragments.

The yellow sulfate also has been noted on dump rock at the Klau and New Idria mines, and it forms thin films on rocks near the exhaust end of the condensing stack at the Mt. Diablo mine in Contra Costa County, California.

ORIGIN

The occurrences of basic mercuric sulfate described previously suggest that it forms by two different processes. In the natural occurrences it is closely associated with cinnabar and is limited to environments exposed to sunlight; on bricks and dumps it occurs in areas suspected of containing elemental mercury as well as cinnabar, and that may not be exposed to sunlight. Even though only one questionable natural occurrence fits the latter environment, similar conditions can under unusual circum-

stances exist in nature and might give rise to appreciable quantities of the mineral through the same process that is responsible for its formation on the dumps.

Because schuetteite forms in the natural occurrences as thin films on cinnabar-bearing surfaces exposed to sunlight, we may conclude that it forms as a result of a reaction involving HgS, sunlight, and a small amount of water containing dissolved oxygen. The surficial water is probably nearly neutral in the mineralized areas where schuetteite occurs, although it may contain locally a little sulfate as a result of limited solution of alunite or the oxidation of pyrite. Some chloride may also be present in the water, but no mercury chlorides or other chlorides have been noted in most of the deposits; even though present chloride would not appreciably aid in dissolving the cinnabar. It thus seems likely the reactions involve only cinnabar, atmospheric oxygen (dissolved in water with a pH a little below 7), and sunlight according to the equation:



The mercuric sulfate with water yields by hydrolysis the basic mercuric sulfate, which has very limited solubility.

If cinnabar, sunlight, oxygen, and water are all that is needed to form the basic mercuric sulfate, one may reasonably ask why the mineral is not more common than it is. The fact that all known occurrences, except the one in the high sulfate environment of Sulphur Bank, are in arid regions suggests the possibility that the amount of sunlight required, or the correct wavelength region of the solar spectrum, or a combination of these two factors, are found only in desert regions. The same explanation can also be applied to the darkening of cinnabar in the sun, which is common in the desert regions yet rarely occurs in the Coast Ranges of California.

The basic mercuric sulfate formed in old furnace bricks and mine dumps is in a high sulfate environment and probably results from the action of strong sulfuric acid solutions on elemental mercury. Although the metal is common in bricks and dumps, it has not been found where the mercuric sulfate is abundant, suggesting it has all been converted to the sulfate. On the other hand the fine-grained cinnabar that occurs with the basic mercuric sulfate on the Oceanic dump appears unetched and unattacked by the solutions that formed the sulfate. In the laboratory, mercuric sulfate can be readily formed by the action of hot concentrated sulfuric acid on mercury but with cold acid the reaction goes very slowly if at all. Preliminary thermodynamic calculations by R. M. Garrels (written communication) suggest mercury sulfate should form only under very strongly acid (pH close to 1) and very strongly oxidizing conditions. Such conditions can occur in nature where pyrite, H₂S, or native sulfur are being rapidly oxidized, but the required pH and Eh are more extreme than is general even in mineralized areas. Under less severe conditions

of acidity and oxidation, native mercury is stable, and probably some native mercury found in oxidizing environments is supergene.

SIGNIFICANCE

Mercuric sulfide is notably more stable in the zone of oxidation than are the sulfides of other common metals, and for this reason opinions differ regarding the possibility of oxidation and secondary enrichment of mercury deposits. Broderick (1916) and Emmons (1917) on the basis of laboratory experiments concluded that cinnabar was essentially insoluble in acid sulfate solutions, but they thought mercury sulfide might be transported in chloride solutions and precipitated as a sulfide by reaction with stibnite or a few other metallic sulfides. Krauskopf (1951) concluded that it was unlikely that HgS could be dissolved appreciably in acid sulfide solutions and indicated that conditions required to effect appreciable solubility with chlorides would seldom, if ever, be met in nature. Examples of cinnabar of supposed supergene origin are discussed by Ross (1942, p. 463-464) who suggests the cinnabar in these places has been mechanically transported as tiny suspended particles.

Saukov and Aidinyan (1940) have described experiments in which ferric sulfate and cinnabar were allowed to stand for periods of as long as 60 days in water containing two drops of sulfuric acid. Tests for ferrous iron and dissolved mercury indicated that the iron was reduced and the HgS oxidized to form HgSO₄, according to the equation:



Similar experiments with NaCl added yielded much larger amounts of ferrous iron and mercury, which was in solution largely as mercuric chloride. As a result of their experiments and field observations, they believed that cinnabar had been leached in the oxidized zone of some mercury deposits.

The occurrence of the basic mercuric sulfate, schuetteite, indicates that under suitable conditions cinnabar can be converted to mercury sulfate, which hydrolyzes almost completely to deposit the insoluble basic mercuric sulfate. As this reaction involves sunlight and is effective only on the surface in restricted areas, and as it results in very little of the mercury sulfate remaining in solution, it is unlikely that any mercury ore body has been appreciably leached or enriched by this process.

The occurrence of the basic mercuric sulfate in considerable quantity in parts of old dumps, where it is believed to have formed as a result of a reaction of sulfuric acid solutions and mercury, suggests that in areas of very strong acidity and oxidation mercury can be taken into solution as a sulfate and can migrate. Such areas in nature will generally occur where there is a large amount of pyrite or marcasite, and in these areas the mercury is normally present as a sulfide rather than as native metal. It there-

fore seems unlikely that the restrictive conditions necessary to bring about leaching of native mercury in the zone of oxidation are often met in nature, although under the most favorable conditions this offers a possible mechanism for leaching of mercury ore bodies.

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MICROSCOPIC CORDIERITE IN FUSED TORRIDONIAN ARKOSE

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ABSTRACT

Progressive thermal metamorphism of Torridonian arkose by a picrite sill in Soay (Hebrides) has culminated in extensive fusion. Microlites of cordierite were precipitated from the liquid as colorless, six-sided prisms (maximum dimension 0.06 mm.) with abundant magnetite inclusions. Refractive indices of the cordierite lie between 1.529 and 1.541, and $(-2V)$ is small. The cordierite is frequently twinned on (110), and rare cruciform twins are also present. The latter have (021) or (101) as the probable twin plane. Only (110) and (130) have been reported previously as cordierite twin planes. The distortion index, Δ (degree of distortion from hexagonal symmetry, measured by x -ray powder diffraction), is 0.08. From independent evidence, the maximum P_{H_2O} was 430 kg/cm², and the minimum temperature interval of cordierite crystallization was 1025° C. to 935° C. If P_{H_2O} were less than 430 kg/cm², the estimated crystallization temperatures would be higher. A useful temperature scale may be established by: (1) correlation of the structural state of cordierite with estimated temperature and pressure of water vapor in buchites, and (2) extension of hydrothermal studies on synthetic cordierites. Both approaches are required because the crystallization history of cordierite may affect its structural state. It is probable that the crystallization histories of cordierites in most buchites followed similar patterns.

INTRODUCTION

Progressive thermal metamorphism of Torridonian arkose by a small picrite sill in Soay (the Hebrides) has culminated in extensive fusion. From the liquid in the fused sediment have crystallized microlites of magnetite, hypersthene, tridymite (now inverted to quartz) and cordierite.* The greatest development of the microlites occurs in black, obsidian-like xenoliths enclosed by the picrite, and it is here that their forms may be readily distinguished. The properties of the cordierite agree with those of the microscopic cordierites which characteristically occur in fused shales and sandstones. Detailed descriptions of such crystals have been presented by Hussack (1883), Prohaska (1885), Zirkel (1891), Harker (1904) and Venkatesh (1952). Records of their occurrence in buchites are too numerous to list. The cordierite in the Soay buchite exhibits cruciform twinning, which has not been reported previously for cordierite.

It has been discovered recently that minerals with cordierite composition exist in several structural modifications (Miyashiro *et al.* 1955). Just

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* A complete account of the metamorphism and fusion will be presented elsewhere.

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as the structural state of feldspars may give some indication of their temperature of formation, so the structural state of minerals with cordierite composition in fused sediments permit an estimate of the temperature of intrusion of the igneous body causing the fusion.

OPTICAL PROPERTIES

The glassy matrix of the fused xenoliths contains minute, colorless, six-sided prisms of cordierite, which constitute a maximum of seven modal per cent of the rocks. Simple prisms are commonly developed (Fig. 1*b*), but parallel growth of somewhat elongated crystals may produce "stepped" edges to the prismatic faces (Fig. 1*c*); in cross section, such crystals appear as overlapping hexagons (Fig. 1*b*). Some crystals are clear while their central parts contain inclusions of dusty magnetite which are arranged parallel to the length of the crystals and which appear as cores in cross sections (Fig. 1*b* and 1*c*). Similar inclusions of spinel or iron ore are common in microscopic cordierites (Prohaska, 1885, Zirkel, 1891, Venkatesh, 1952). In the glass surrounding many cordierite crystals there are cracks either approximately perpendicular to the crystal edges (Fig. 1*c*), or following approximately the crystal boundaries (Fig. 1*b*, cf. Zirkel, 1891). The cracks probably developed during cooling by contraction of the glass away from the cordierite.

Even with very fine crushing it was impossible to obtain crystals free from glass and it could be determined only that the refractive indices of the cordierite lie between 1.529 and 1.541 (± 0.003). All prismatic sections have straight extinction and most are length fast. The few which are length slow probably represent very short prisms with the diameter of the basal pinacoid greater than the length of the prism faces (Prohaska, 1885, Zirkel, 1891). Pseudo-hexagonal sections are almost isotropic but sector twinning is visible in many sections. The twinning can be seen more clearly if the mineral is viewed in sodium light with a retardation plate inserted. There are six triangular sectors with opposite pairs in optical continuity, and the slow vibration direction is perpendicular to the prism face in each sector. The twin plane and composition plane is therefore (110) (Venkatesh, 1952). The optic axial plane is perpendicular to the prism face in each sector and the optic orientation of the twinned crystals is that illustrated in Winchell and Winchell (1951, figure 364). Attempts to measure 2V on the universal stage were unsuccessful but since basal sections are almost isotropic, $(-)2V$ must be small.

At least one crystal in a fused xenolith has the shape of a cruciform twin. The insertion of a one wave length retardation plate renders the twin units clearly visible (Fig. 1*e*). Two other crystals were found which appeared similar (Fig. 1*b*), but they were too small for details to be dis-

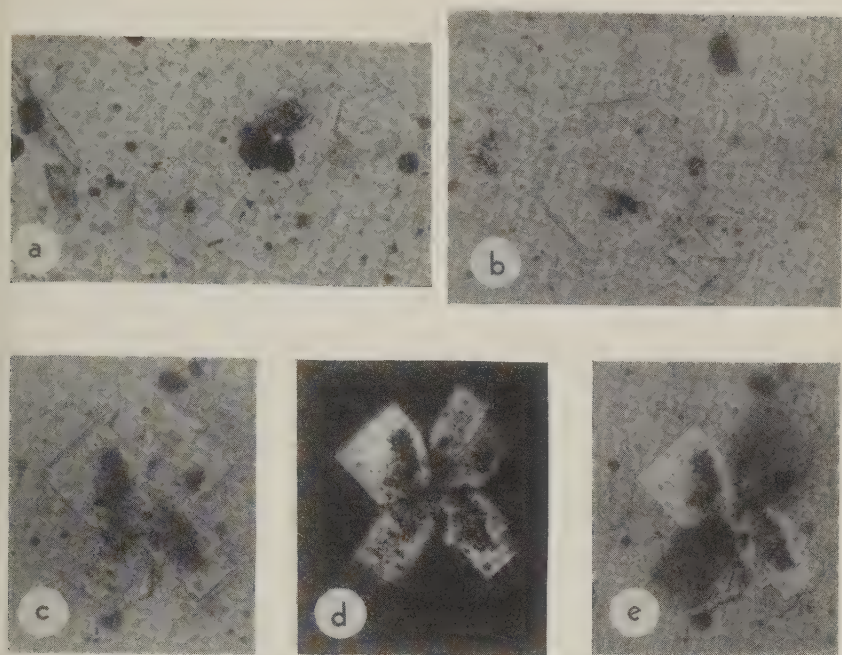


FIG. 1. Thin sections of buchite enclosed by picrite ($\times 400$). The groundmass of glass contains microlites of cordierite, hypersthene and magnetite. (a) Plain light; sections through six-sided prisms of cordierite; also present are accicular hypersthene and equant magnetite. (b) Plain light; six-sided cross-section of a large cordierite prism, partially surrounded by a crack in the glass. To the left is a small six-sided prism, with magnetite inclusions, lying completely within the thickness of the section. In the upper right corner is a poorly defined cruciform twin. (c) Plain light; cruciform twin of cordierite with abundant magnetite inclusions. The "stepped" edges to prismatic faces result from parallel growth along the 'c' axis. In the glass surrounding the crystal there are small cracks perpendicular to the crystal edges. (d) The same as (c), with nicols crossed. The prisms are approximately 45° from extinction. (e) The same as (d) with a one wave-length retardation plate inserted in the 45° position. This demonstrates the different optical orientations of the twin units. The probable twin plane is either (021) or (101).

tinguished. On the universal stage, the approximate positions of two optic symmetry planes, both containing the 'c' axis, were determined for each twin unit. It could not be ascertained which of these was the optic axial plane because no optic axes were located. From stereographic projection of the data the most probable twin plane is either (021) or (101), depending upon which of the optic symmetry planes is the optic axial plane. These are twin planes which have not been reported previously for cordierite. According to Winchell and Winchell (1951) and Venkatesh (1954), twinning in cordierite is exclusively confined to the (110) and

(130) planes, and twinning on (130), as well as (110), produces sector twinning in basal sections. In recent hydrothermal experiments on the fusion of shales (Wyllie and Tuttle, 1958) it was found that cordierite which grew in the fused charges invariably contained a small proportion of crystals exhibiting cruciform twins similar to those illustrated in Fig. 1. Careful search in buchites will probably reveal other examples and perhaps some can be found which will permit more accurate crystallographic measurements.

STRUCTURAL STATE

Miyashiro and others (1955, 1957) have recently discovered that crystals of cordierite composition exist in at least three structural modifications—indialite, high cordierite, and low cordierite. The new high temperature hexagonal mineral, indialite, was found among cordierites developed in sediments fused by burning coal seams (the cordierite was described by Venkatesh 1952, 1954). Apparently all gradations exist between hexagonal indialite and orthorhombic cordierite through distortion of the hexagonal lattice, and the distortion is probably caused by ordering of Si and Al atoms. Although the thermal relations existing among the polymorphs have been investigated, much experimental work remains to be completed.

The degree of distortion of the hexagonal lattice in cordierites can be measured easily on an x -ray powder diffraction pattern, and an angle representing the difference in 2θ between two peaks (CuK α radiation) was called the distortion index, Δ , by Miyashiro (1957). For hexagonal indialite there is only one peak and the distortion index Δ is 0. For the most distorted cordierites Δ reaches 0.3. Δ was measured for the cordierite in the Soay buchite; the cordierite was not separated from glass and other minerals in the specimen, and Δ was determined from x -ray powder diffraction patterns of composite samples. Cordierite amounts to only seven modal per cent of the specimen, but satisfactory peaks were obtained in the required region. Diffraction patterns were recorded for several different samples. In most patterns the two peaks were not clearly resolved, but in others two peaks were obtained, and a value of $\Delta=0.08$ was measured. This indicates that the symmetry of the cordierite is nearly hexagonal (this is confirmed by its small $2V$).

The structural state of minerals with cordierite composition may yield information about their temperatures of crystallization. If equilibrium is maintained the least ordered forms would be expected from high temperature environments and the most ordered forms from low temperature environments. However, this simple picture is complicated by the fact that high and low forms may be distinguished regardless of the structural

state. There is also another difficulty, namely that the structural state of cordierite will depend not only upon its temperature of crystallization, but also upon its crystallization history. Moreover, Miyashiro (1957) points out that many natural disordered cordierites have crystallized metastably at low temperatures.

Before we can infer growth conditions from measurements on natural cordierites, it is important that the structural state of cordierite be related under equilibrium conditions to varying temperatures and pressures of water vapor. Such studies are under way at the Geophysical Laboratory (personal communication from W. Schreyer). However, even when this work is completed, the distortion index of natural cordierites will not always be a satisfactory index of PT conditions, because (1) cordierite can crystallize in a metastable structural state, and (2) cordierite has so many structural holes that different environments may have a marked influence on the structural state in which it crystallizes. We cannot afford to neglect the crystallization history of such a mineral. For cordierites which have similar crystallization histories there is probably a simple correlation between temperature, pressure, and structural state. Most buchites contain cordierite and it is likely that their crystallization histories followed similar patterns: buchites are generally associated with hypabyssal intrusions, there is evidence that fusion proceeded in the presence of abundant water vapor, the cordierite crystallized from a liquid of granitic composition, rapid cooling is indicated by the preservation of glass and, finally, high cordierite always crystallizes in this environment. There remains to be considered the influence of compositional variation. According to Iijama (1956) there is no simple relation between the optical properties and the compositions of cordierite unless special attention is paid to structural relationships. Using Iijama's data, the cordierite in the Soay buchite appears to be rich in magnesium and poor in iron and manganese. Comparison of the mode and chemical analysis of a fused xenolith containing cordierite confirms that the cordierite is magnesian because the amount of iron present is barely sufficient to account for the modal magnetite. It seems probable that the cordierite developed in buchites is generally rich in magnesia, except in the rare cases where the fused sediment is unusually rich in iron.

Measurements of the distortion index of cordierites from buchites may therefore provide a good indication of PT conditions, but care must be exercised in relating these measurements to equilibrium data obtained in laboratory experiments, because the two environments are very different. It is necessary first to obtain independent estimates of PT conditions in natural occurrences to provide a correlation between the laboratory and field measurements.

CONDITIONS OF FORMATION

For the Soay buchite an estimate of the temperature of the liquid from which the cordierite crystallized is available (Wyllie, 1958). The compositions of the liquids present in the xenolith at the stages of maximum fusion and of quenching were calculated from chemical and modal analyses of a fused xenolith. Liquidus temperatures for these compositions were estimated from experimental data in the system albite-orthoclase-quartz-water for various pressures of water vapor (Tuttle and Bowen, 1958), and in this way, PT curves for the calculated liquid compositions were derived (AB and CD, Fig. 2). Since tridymite crystallized from the liquid, an upper pressure limit for the fusion was obtained from the intersection of the experimentally determined PT curve for the inversion of tridymite to quartz (in the presence of excess water vapor) with the curve CD. The range of PT conditions accompanying the cooling and crystallization of the liquid developed in the xenolith lies between the two PT curves AB and CD with temperatures between 1025° C. and 935° C. at a pressure of 430 kg./cm.² of water vapor, and between 1310° C. and 1225° C. at atmospheric pressure. Without an independent estimate of pressure, no closer estimate of the temperature range can be made. Assuming that the total pressure equalled the pressure of water vapor (which is probable in this example), the upper pressure limit (AC) corresponds to a depth of about 1.7 km., and it is unlikely that the picrite sill was emplaced much higher in the crust than this.

The cordierite in the Soay buchite, with distortion index of 0.08, therefore crystallized within a PT range close to the line AC of Fig. 2. The equilibrium PT conditions determined hydrothermally which correspond to a distortion index of 0.08 may differ from the estimate derived in this section. But if several independent estimates of this sort can be made it may be possible to obtain a correction factor for cordierite *in this environment* which could be applied to the experimental data. If this proves feasible, we would have a simple method for estimating the temperature and pressure at the contacts of hypabyssal igneous intrusions when buchite is developed. An x-ray powder diffraction pattern of a crushed sample of the buchite, giving directly the distortion index of the cordierite, is the only measurement involved.

This data is presented as a first step toward the correlation of laboratory data with the properties of cordierite in buchites. Here we have an ultrabasic sill against which buchite has developed. The cordierite in the buchite has a distortion index of 0.08, and an independent estimate of PT conditions gives a crystallization range near to the line CD in Fig. 2. It is important that we check back and forth from rocks to experiments very

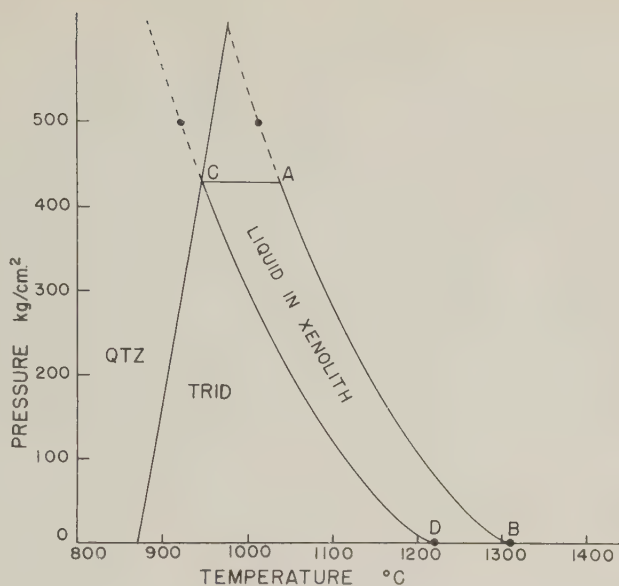


FIG. 2. Estimate of the PT conditions when the cordierite crystallized. The stage of maximum fusion of the xenolith is represented by the curve AB, and the condition when the liquid was quenched to a glass is represented by the curve CD. An upper pressure limit is given by the intersection of the quartz-tridymite inversion (in the presence of excess water vapor) with the curve CD. Cordierite crystallized from the liquid in the fused xenolith at PT conditions within the area ABCD, and probably close to the line CA.

frequently if we are to obtain full benefit from the increasing amount of controlled experimental data now becoming available.

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NEW DATA ON GASTUNITE, AN ALKALI URANYL SILICATE

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ABSTRACT

Gastunite is an alkali uranyl silicate with the composition $(K, Na)_2(UO_2)_3(Si_2O_5)_4 \cdot 8H_2O$. Chemical analysis, recalculated after deducting impurities, gives SiO_2 —31.2, UO_3 —53.8, K_2O —4.6, Na_2O —0.9, H_2O —9.5, total 100.0 per cent. The proposed formula is supported by infra-red absorption data. X-ray study shows the mineral to be orthorhombic, space group *Pnna* (W. Outerbridge), a_o —14.24, b_o —35.84, c_o —14.20, calculated specific gravity 3.97 (3.96 ± 0.03 measured). Indexed powder pattern shows the strongest lines to be 7.12 (10), 3.56 (9), 9.10 (8), 4.83 (7), 3.31 (7). Optically biaxial positive with $\alpha=1.604$, $\beta=1.610$, $\gamma=1.621$: 2V moderate, anomalous blue interference color. Habit: radiating acicular to fibrous aggregates. Hardness 2. Perfect (010) cleavage. Gastunite occurs as a secondary mineral in radial aggregates coating chalcedony at the Red Knob mine, Muggins Mountains, Yuma County, Arizona; and in vesicular cavities in welded tuff at the Mammoth prospect, Presidio County, Texas. Also present in dense fine-grained pseudomorphs after uraninite from the Easton area, Pennsylvania. Hydrothermal synthesis data for the potassium, potassium plus sodium, sodium, ammonium, and hydronium analogues of gastunite are presented.

INTRODUCTION

Systematic investigation of secondary uranium minerals in the Harvard collection as part of a research project concerning the uranyl silicate minerals has revealed a second potassium uranyl silicate. The mineral is similar to uranophane in general aspect and occurrence, but on close examination is quite distinct in all respects. The mineral was first noted by Professor Clifford Frondel on specimens from the Red Knob mine, Muggins Mountains, Yuma Co., Arizona; and soon thereafter on specimens from the Mammoth prospect, Presidio Co., Texas, and the Easton area, Pennsylvania.

A search of the literature on the uranyl silicate minerals reveals that this new mineral bears a striking resemblance to gastunite, a provisional description of which was published by Haberlandt and Schiener (1951). More complete data is here presented, and a comparison made with the original data for gastunite.

HABIT, PHYSICAL PROPERTIES, AND OPTICS

Gastunite occurs as radial aggregates of acicular to fibrous crystals coating cavities, and in the Easton material as a dense microcrystalline aggregate pseudomorphous after uraninite. The color varies from yellow to greenish yellow in the radial aggregates, and is a dull straw yellow in the dense material. The specific gravity, determined from three fragments of the radial aggregates is 3.96 ± 0.03 (3.97 calculated). Hardness 2.

There is a perfect (010) cleavage. Luster vitreous to pearly. The mineral does not fluoresce under either long- or short-wave ultraviolet excitation.

Optical data are listed in Table 1. Specimens of the Easton, Pennsylvania material and of the synthetically prepared material are seen on optical examination to be extremely fine-grained, and yield only an average index of refraction.

X-RAY DATA

The small grain size of material available to the writer precluded morphological and single crystal x-ray study, but it was found that the powder diffraction pattern could be indexed on a tetragonal cell. Resolution of the unit cell problem was made possible by data supplied from electron diffraction studies by W. Outerbridge of the U. S. Geological Survey (M. H. Staatz, personal communication). Outerbridge found the mineral to be orthorhombic, with marked pseudotetragonal symmetry.

TABLE 1. OPTICAL DATA

Analysis sample—Red Knob mine, Muggins Mountains, Yuma Co., Arizona		
α —1.604	Colorless	Biaxial positive
β —1.610	Very pale yellow	2V—moderate
γ —1.621	Pale yellow	Anomalous blue interference color
		Parallel extinction
		Elongation = Z
Mammoth prospect, Presidio Co., Texas		
α —1.596	Colorless	Biaxial positive
β —1.605	Very pale yellow	2V—large
γ —1.620	Pale yellow	Anomalous blue interference color
		Parallel extinction
		Elongation both parallel to and perpendicular to Z
Thomas Range, Utah (M. H. Staatz, personal communication)		
α —1.596		
β — —		
γ —1.606		
Easton, Pennsylvania		
Average n —1.61		
Synthetic products (too fine-grained for complete optical data):		
Potassium gastunite—average n —1.62. Anomalous blue.		
Potassium plus sodium gastunite—average n —1.611.		
Sodium gastunite—average n —1.61.		
Ammonium gastunite—average n —1.604.		
Hydronium gastunite—average n —1.601.		

TABLE 2. X-RAY CRYSTALLOGRAPHIC DATA

Gastunite—Orthorhombic (pseudotetragonal), space group Pnna, $a:b:c=0.39732:1:0.39621$. Calculated S. G. 3.97 (measured 3.96 ± 0.03). $Z=11$.

<i>Honea</i>	<i>Outerbridge</i>
$a-14.24 \pm 0.01A$	$14.26 \pm 0.05A$
$b-35.84 \pm 0.02A$	$35.88 \pm 0.10A$
$c-14.20 \pm 0.01A$	$14.20 \pm 0.02A$

Table 2 compares the data of Outerbridge with that of the writer, whose information was obtained from an indexed powder pattern. Spacings on the powder pattern are given in Table 3.

ANALYTICAL DATA

X-ray fluorescence analyses were made of material from the Texas and Arizona localities (Table 4), and a quantitative chemical analysis made by Jun Ito of the Harvard Mineralogical Laboratory on the material from Arizona. Great difficulty was encountered in separating sufficiently pure material for analysis, and it became necessary to compromise on a sample containing known impurities of wulfenite, vanadinite, and cuprite. The separation was accomplished by coarse grinding of material flaked off the specimen and subsequent removal of larger grains of impurities. The portion remaining was then separated in methylene iodide (S. G. 3.29) and the light fraction rejected. The heavy fraction was then ground slightly finer (-60 mesh), rerun through the heavy liquid, and then carefully hand-picked under the binocular microscope. It immediately became obvious that a complete separation was impossible because certain of the impurities were intimately intergrown with and included in the gastunite. For this reason enough of each visible impurity was taken for preparation of a powder spindle for identification and subsequent subtraction from the analysis.

Results of the chemical analysis are given in Table 5. Molecular amounts of the principal components after recalculation of the analysis indicate a composition of $(K, Na)_2O \cdot 3UO_3 \cdot 8SiO_2 \cdot 8H_2O$. The analysis, infra-red absorption data, and physical properties suggest a phyllosilicate formula, $(K, Na)_2(UO_2)_3(Si_2O_5)_4 \cdot 8H_2O$.

INFRA-RED ABSORPTION SPECTRA

Infra-red absorption data was obtained using a Perkin-Elmer instrument with sodium chloride prism. Samples were prepared for analysis by pressing a wafer containing 5 mg of very finely ground mineral in 0.7 grams of potassium bromide mounting medium. Since not enough ma-

TABLE 3. INDEXED POWDER PATTERN OF GASTUNITE. ORTHORHOMBIC (PSEUDO-TETRAGONAL), SPACE GROUP Pnna (W. OUTERBRIDGE), a_0 —14.24, b_0 —35.84, c_0 —14.20. Cu RADIATION, Ni FILTERED, WAVELENGTH 1.5418 Å

d_{meas}	I	hkl	d_{calc}	d_{meas}	I	hkl	d_{calc}	d_{meas}	I	hkl	d_{calc}
9.10	8	031	9.14			2111	2.90	2.18	2	1161	2.19
7.12	10	200	7.12			1112	2.90			4130	2.18
		002	7.10	2.81	2	462	2.81			661	2.18
6.59	1	220	6.62			3101	2.80			642	2.18
		022	6.60			392	2.80			4122	2.18
5.57	7	042	5.57	2.51	3	0104	2.52	2.10	4	0170	2.11
		240	5.57			404	2.51			662	2.11
4.83	3	071	4.82			3112	2.51			3151	2.11
4.58	5	260	4.58	2.41	4	562	2.42			680	2.10
		062	4.57			2132	2.42			0171	2.09
4.45	2	311	4.45			0142	2.41			086	2.09
3.84	5	322	3.85			2140	2.41	1.991	3	4142	1.995
		262	3.84			4110	2.40			0180	1.991
		091	3.83	2.38	5	0150	2.39			731	1.986
3.56	9	400	3.56			0133	2.38	1.973	4	0106	1.975
		004	3.55			2141	2.38			604	1.973
3.31	7	440	3.32			4102	2.38			406	1.971
		431	3.31			3122	2.38	1.927	3	732	1.930
3.18	7	450	3.19			600	2.37			0173	1.923
		402	3.18	2.29	5	006	2.37	1.903	5	6111	1.901
		204	3.18			631	2.30			2181	1.900
		381	3.18			046	2.29			1102	1.900
		0111	3.18			4120	2.29	1.872	2	0191	1.870
		412	3.17			640	2.29			4161	1.869
3.13	1	222	3.17			591	2.29	1.830	2	4162	1.832
		422	3.13	2.24	3	582	2.28			0155	1.828
		372	3.13			602	2.25			772	1.827
		292	3.12			206	2.25	1.778	4	800	1.780
		2101	3.12			0160	2.24			3182	1.778
		1102	3.12			2151	2.24			008	1.775
2.99	4	442	3.00			1152	2.24	1.743	3	6132	1.744
		461	2.99	2.20	4	651	2.23			048	1.741
		0120	2.99			632	2.21			3191	1.740
		391	2.98			066	2.20	1.725	4	6141	1.728
2.91	7	470	2.92			660	2.20			802	1.727
		2102	2.92			5101	2.20			208	1.722
		452	2.91			592	2.20			0117	1.722

d_{meas}	I	d_{meas}	I	d_{meas}	I	d_{meas}	I
1.689	4	1.322	3	1.088	$\frac{1}{2}$	0.903	$\frac{1}{2}b$
1.658	3	1.298	2b	1.063	1b	0.861	$\frac{1}{2}b$
1.592	3b†	1.260	1b	1.052	1	0.858	$\frac{1}{2}b$
1.562	4b	1.244	2	1.029	1	0.812	$\frac{1}{2}b$
1.518	1b	1.226	1	1.018	2	0.805	1
1.481	$\frac{1}{2}$	1.188	2b	0.989	1b	0.797	$\frac{1}{2}b$
1.458	1	1.174	2	0.979	1	0.794	$\frac{1}{2}b$
1.431	2b	1.154	1	0.968	1	0.791	$\frac{1}{2}b$
1.404	3	1.125	$\frac{1}{2}$	0.952	1b	0.779	$\frac{1}{2}b$
1.384	1	1.113	2	0.935	1	0.777	$\frac{1}{2}$
1.357	1b	1.101	1	0.912	$\frac{1}{2}$		

† b=broad.

TABLE 4. X-RAY FLUORESCENCE ANALYSIS OF GASTUNITE
FROM ARIZONA AND TEXAS

Red Knob mine, Muggins Mountains, Yuma Co., Arizona
Major—U
Minor—Pb, Mo, V, Cu, Fe
Mammoth prospect, Presidio Co., Texas
Major—U
Minor—Ba, Fe

terial was available from the chemical analysis sample, data from the Presidio County, Texas material is compared with that of synthetic products in Figure 1.

All three absorption spectra show maxima near 3.0 and 6.2 microns that correspond to the stretching and bending vibrations respectively of the hydroxyl (or HOH) bond (Randall, *et al.*, 1949). The absorption curve for ammonium gastunite (Figure 1C) also has lower wavelength

TABLE 5. CHEMICAL ANALYSIS OF GASTUNITE FROM THE RED KNOB MINE, MUGGINS
MOUNTAINS, YUMA CO., ARIZONA. ANALYST JUN ITO

	A	B	C	D	E	F
SiO ₂	23.1	3,846	31.2	5,195	8.21	30.47
UO ₃	39.8	1,391	53.8	1,881	2.97	54.42
K ₂ O	3.4	361	4.6	488	1.00	5.97
Na ₂ O	0.7	113	0.9	145		
H ₂ O	7.0	3,885	9.5	5,273	8.33	9.14
CaO	1.1	196	—			—
PbO	11.4	511	—			—
MoO ₃	7.2	500	—			—
V ₂ O ₅	0.6	33	—			—
Cu ₂ O	1.2	84	—			—
MnO	0.2	28	—			—
Fe ₂ O ₃	0.3	19	—			—
Rem.	2.9		—			—
Total	98.9		100.0			100.00

A. Analysis of sample containing known impurities of wulfenite, vanadinite, cuprite and "limonite." Rem., determined by semi-quantitative spectrographic analysis on 3 mg. of material, contains NiO—0.03, CoO—0.x, ZnO—0.X (Zn>Co), MgO—0.0X, Cr₂O₃—present, ZrO₂—present, TiO₂—present, In and Tl—present.

B. Molecular amounts calculated from analysis.

C. Principal components of gastunite recalculated to 100% after deducting impurities.

D. Molecular amounts for recalculated analysis.

E. Molecular proportions.

F. Theoretical composition of K₂(UO₂)₃(Si₂O₅)₄·8H₂O.

peaks at 3.2 and 7.15 microns, the stretching and bending vibrations characteristic of the ammonium ion (Bellamy, 1954). Strong absorption in the region from 9 to 12 microns includes the wavelengths of 9.4 to 10.4 microns shown by Launer (1952, p. 782) to be typical of silicate bonding of the phyllosilicate type.

Comparison with Launer's data might also lead one to suspect a single chain structure (maxima in region from 9.2 to 11.6 microns)

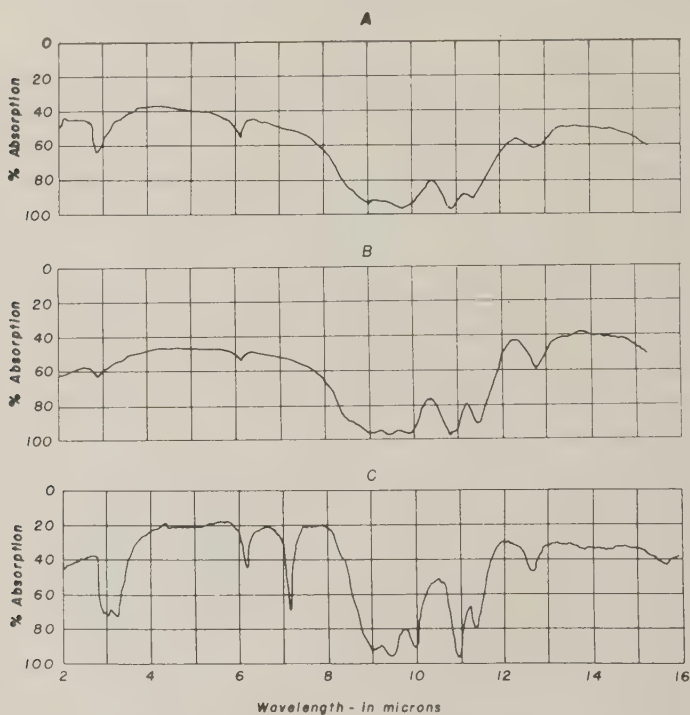


FIG. 1. Infrared-absorption spectra of natural and synthetic gastunite. A. Gastunite—Mammoth prospect, Presidio County, Texas. B. Synthetic potassium gastunite. C. Synthetic ammonium gastunite.

except that the chemical analysis shows there to be insufficient cations to balance the resulting anion charge. Shifts from the wavelengths cited by Launer (1952, p. 781) may result from differences in bond energies in uranyl silicate minerals as compared to the clay and mica minerals from which his data are taken. Also, Bellamy (1954, p. 309) tentatively assigns an absorption maximum near 11 microns to the uranyl ion, adding further to a resemblance of the above spectra to that of the phyllosilicates.

SYNTHESIS

Gastunite was first synthesized by the writer in July, 1956, and has since been noted as a synthetic product by A. M. Pommer (personal communication). The mineral has been prepared in low temperature runs (90° C.) by coprecipitation of soluble salts containing the essential ions. Precipitation is accomplished by raising the pH using NH_4OH or other similar base. The mineral persists in hydrothermal bomb runs to 250° C., becoming slightly more coarsely crystalline in runs allowed to heat for two weeks. Unfortunately the writer has not succeeded in obtaining crystals large enough for complete optical data.

As shown in Table 6 the potassium, potassium plus sodium, sodium, ammonium, and hydronium analogues of gastunite have been prepared in the laboratory. It will be noted in the table that gastunite appears in runs containing divalent cations, but the divalent cations are not believed essential to the structure. All of the analogues listed above yield x-ray powder patterns with essentially identical spacings and only slightly different intensities than those of the natural mineral as listed in Table 3.

Boltwoodite, the first of the alkali uranyl silicates to be described (Fondel and Ito, 1956), appears in some of the above syntheses. It is significant that boltwoodite is consistently the stable phase at higher pH when it does appear. Contrary results have been noted by A. M. Pommer (personal communication), but his method of synthesis is quite different and composition of the system would be expected to influence stability relations.

OCCURRENCE

The occurrence of the Easton, Pennsylvania material as pseudomorphs after uraninite indicates a definite secondary origin for gastunite, and by analogy with this occurrence and that of the other uranyl silicate minerals (Fondel, 1956) a similar origin is proposed for the better crystallized material from the other two localities studied by the writer. The Texas and Arizona material show no trace of original uraninite, and it is believed that the component ions were transported for short distances and deposited in cavities. The associated minerals; chalcedony, wulfenite, vanadinite, cuprite, and "limonite" in the Arizona specimen; and uranophane with smaller amounts of sklodowskite in the Texas specimen also indicate a secondary origin.

Specimens from the Red Knob mine, Muggins Mountains, Yuma County, Arizona, typically have gastunite as radial aggregates of acicular crystals coating, and intergrown with, the minerals listed above. The

TABLE 6. SYNTHESIS OF GASTUNITE

Reagents	pH	Temp.	Product	Bomb Run	pH	Product
Potassium silicofluoride Uranyl acetate Potassium hydroxide	8	90°	Boltwoodite	48 hrs. @ 235°	7	Potassium gastunite Boltwoodite
Potassium silicofluoride Uranyl acetate Potassium hydroxide	8	90	Boltwoodite	46 hrs. @ 243	6	Potassium gastunite
Sodium metasilicate Uranyl acetate Potassium acetate Potassium hydroxide	8	90	Amorphous	48 hrs. @ 249	7	Potassium-sodium gastunite
Ammonium silicofluoride Uranyl acetate Sodium acetate Sodium hydroxide	7½	90	Sodium gastunite	48 hrs. @ 235	6	Sodium gastunite
Potassium silicofluoride Uranyl acetate Sodium hydroxide	7½	90	Boltwoodite	48 hrs. @ 240	7	Sodium-potassium gastunite
Sodium orthosilicate Uranyl acetate Calcium acetate	11	85	Amorphous	48 hrs. @ 235	7	Sodium gastunite
Ammonium silicofluoride Uranyl acetate Ammonium hydroxide	7	90	Ammonium gastunite	48 hrs. @ 152	6	Soddyite
Sodium metasilicate Uranyl acetate Calcium acetate Ammonium hydroxide	8	95	Ammonium gastunite	41 hrs. @ 230	8½	Soddyite
Ammonium silicofluoride Uranyl acetate Lead acetate Ammonium hydroxide	8	95	Ammonium gastunite	48 hrs. @ 235	5	Kasolite
Ammonium silicofluoride Uranyl acetate Magnesium acetate Ammonium hydroxide	7	95	Ammonium gastunite	45 hrs. @ 252	5½	Hydronium gastunite
Ammonium silicofluoride Uranyl acetate Strontium acetate Ammonium hydroxide	7	90	Ammonium gastunite	48 hrs. @ 246	5	Hydronium gastunite Strontium fluoride

Mammoth prospect, Presidio County, Texas, material occurs as a lining of acicular to fibrous gastunite in vesicular cavities in a welded rhyolite tuff. The mineral occurs in a more highly bleached portion of the rhyolite, and is slightly deeper in color than the more abundant uranophane

of the area. Chalcedonic and opaline quartz are also present in the cavities. Staatz (oral communication), who first noted the mineral several years ago from the Easton locality, has noted several localities unknown to the writer. These include several mines and prospects in the Thomas Range, Utah, and localities in California and Mexico.

COMPARISON WITH ORIGINAL DATA FOR GASTUNITE

It appears likely that the mineral herein described is identical with gastunite as provisionally described by Haberlandt and Schiener (1951). The lack of x-ray and analytical data in the original description makes

TABLE 7. COMPARISON OF PRESENT DATA WITH PUBLISHED DATA FOR GASTUNITE

	Gastunite			Present mineral
Color	Greenish yellow			Yellow to citron yellow
Crystal habit	Radial aggregate of needle-like crystals			Radial aggregates of acicular to fibrous crystals
Optics	nX—1.596 nY nZ—1.597	Colorless to pale yellow Darker citron yellow	Anomalous blue Elongation =Z	nX—1.596–1.604 Colorless nY—1.605–1.610 Pale yellow nZ—1.606–1.622 Pale yellow to greenish yellow Biaxial (+), anomalous blue, Z either 11 or $\perp$ to elongation
Composition	Spectrographic analysis—main components U, Ca, Si, Pb			Chemical analysis—main components U, Si, K, Na. Ca present, but is non-essential
X-ray powder pattern	Not identifiable with any other			Distinct from all known uranyl silicates

a precise comparison impossible, but the available information is summarized in Table 7. The habit, occurrence, and optical data indicate the probable identity.

Gastunite occurs at the hot springs at Bad Gastein, Salzburg, and is named from the locality.

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THE PREPARATION AND PROPERTIES OF URANIUM (IV) SILICATE*

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ABSTRACT

Uranium (IV) orthosilicate, corresponding to the mineral coffinite, has been synthesized by a hydrothermal procedure. Preparative conditions including precipitation techniques, temperature, pH and uranium oxidation state have been investigated. USiO_4 is a blue microcrystalline compound isostructural with thorite and zircon. The infrared spectrum of USiO_4 shows an absorption maximum at 11.1μ , characteristic of isolated SiO_4^{4-} tetrahedra. No evidence was found for hydroxyl substitution in the synthetic material. USiO_4 is stable to 1000°C . in a vacuum and to 500°C . in air.

INTRODUCTION

Zircon and thorite are well-known mineral constituents and procedures have been established for their synthesis in the laboratory. The two orthosilicates are isostructural, crystallizing with tetragonal symmetry. Until recently the uranium (IV) analogue had not been found in nature nor prepared in the laboratory. Partial substitution of uranium for thorium is frequently observed (uranothorites), but the uranium content rarely exceeds 10%.

Recently a preliminary announcement by Stieff, Stern and Sherwood (1955) reported the discovery of a new uranium mineral in the LaSal No. 2 mine on the Colorado Plateau. The mineral, isostructural with zircon and thorite, was given the name coffinite. A later more detailed, description (1956) characterized the substance as a uranous silicate (ideally USiO_4) with partial substitution of $(\text{OH})_4^{4-}$ for $(\text{SiO}_4)^{4-}$. At approximately the same time Hoekstra and Fuchs (1956) announced the synthesis of USiO_4 in the laboratory. Fuchs and Gebert (1958) have subsequently reported detailed x-ray diffraction results on coffinite, thorite and uranothorite. The present paper will describe in greater detail the preparation of coffinite and some of its properties.

PREPARATION OF USiO_4

According to Iler (1955) an insoluble metal silicate is usually precipitated as a gelatinous amorphous mass when a solution of a polyvalent metal salt is added to a solution of a soluble alkali metal silicate. Maurice (1949) reported the hydrothermal preparation of zircon by heating amorphous zirconium silicate in acid or weakly alkaline solutions. We have used an analogous procedure for the synthesis of coffinite, but find that the uranium compound is obtained only in basic solutions. The uranium-

* Based on work performed under the auspices of the U. S. Atomic Energy Commission.

silicate solution is prepared by dissolving equimolar quantities (one millimole each) of uranium (IV) tetrachloride and sodium metasilicate in distilled water (10 ml). Sodium hydroxide solution (1 *M*) is then added dropwise until a stiff green gel forms near the neutral point. The gel is broken by adding a few additional drops of base with shaking. When sufficient base has been added to make the solution slightly alkaline, the gelatinous precipitate is centrifuged and the supernate decanted to a total volume of approximately 6 ml. The preparation is then buffered to a pH 8.3 by adding sufficient sodium bicarbonate to make a 0.5 *M* solution. Excess silica is provided by adding powdered vitreous silica (0.25 gm.). The slurry is poured into a platinum cup which is then inserted into an Inconel hydrothermal reaction vessel (11 ml. capacity) fitted with a compression seal. All operations are performed in a nitrogen atmosphere to prevent oxidation of tetravalent uranium. The sealed reaction vessel is heated 24 hours at 250° C. or 120 hours at 200° C. The pressure in the reaction vessel has not been determined, but is assumed to be approximately equal to the vapor pressure of water at the given temperatures (15 atm. at 200° C., 40 atm. at 250° C.). The synthetic coffinite is obtained as a microcrystalline solid which may be separated from the bulk of the excess silica (as quartz) by gravitational methods in water. Despite its lower density the bulk of the quartz settles more rapidly than the extremely finely-divided coffinite.

FACTORS INFLUENCING COFFINITE SYNTHESIS

Precipitation Technique

It has been shown (Iler, 1955) that most solutions of soluble silicates contain a mixture of polysilicate ions. Since these ions are not of uniform size, they cannot form a regular crystal lattice when precipitated with metal ions. In order to obtain a crystalline silicate the polysilicate ions must be depolymerized in order to rearrange themselves into a regular lattice. Thus, precipitation of a metal silicate solution at ordinary temperature usually results in a colloidal mixture of metal ions on gelatinous silica or as a mutual coagulation of positively charged colloidal metal hydroxide and negatively charged colloidal silica. Britton (1927) also concluded that mutual coagulation rather than compound formation occurs on precipitation of metal hydroxides with sodium silicate. Based on these observations, it appears that depolymerization of the polysilicate and formation of USiO_4 occurs during the heating process rather than during the precipitation step. Co-precipitation of uranium and silica is necessary for the synthesis, since the mixing of freshly prepared uranium (IV) hydroxide and silica results in the formation of uraninite and quartz, even though all other conditions of the experiment are

identical. This suggests that coffinite in nature is not likely to be formed by the reaction of finely-divided UO_2 and colloidal silica. Instead, the reaction probably involves dilute solutions containing soluble monomeric silica. The frequent association of coffinite with organic material also suggests that reduction of solutions containing hexavalent uranium, followed by precipitation as the orthosilicate may occur.

pH and Buffers

An alkaline environment appears to be essential for the laboratory synthesis of coffinite. Because of the uncertainty of pH maintenance in

TABLE 1. EFFECT OF pH AND BUFFERING AGENTS ON COFFINITE PREPARATION
Solutions heated 115 hours at 250° C.

Buffer	pH before heating	pH after heating	Products
None	10	8.9	diffuse UO_2
None	6.6	7.3	diffuse UO_2
None	6.7	6.6	diffuse UO_2
None	7.5	8.7	mostly coffinite+diffuse UO_2
None	9.9	10.1	coffinite
0.5 M $\text{Na}_2\text{B}_4\text{O}_7$	9.3	9.0	mostly coffinite+diffuse UO_2
0.1 M Na_2CO_3	10.7	10.2	mostly coffinite+diffuse UO_2
0.2 M Na_2CO_3	10.7	9.5	mostly coffinite+quartz+ UO_2
0.1 M Na_2SiO_3	11.4	11.2	no coffinite, unknown compound
0.1 M NaHCO_3	8.8	8.8	mostly coffinite+diffuse UO_2
0.5 M NaHCO_3	8.4	8.1	mostly coffinite+quartz
0.6 M KH_2PO_4	8.2	8.6	diffuse UO_2 +quartz
0.04 M $\text{Na}_4\text{B}_4\text{O}_7$			
0.05 M KH_2PO_4			
0.05 M $\text{Na}_2\text{B}_4\text{O}_7$	8.6	8.6	diffuse UO_2 +quartz

non-buffered solutions, synthesis could be repeated effectively only when buffering was provided. The effect of pH and various buffering agents is illustrated in Table 1. The pH limits for successful preparation of USiO_4 lie between 8 and 10.5.

Temperature

Coffinite is crystallized after heating a standard preparation (as described above) for 24 hours at 250° C., and a mixture of coffinite with trace amounts of UO_2 is obtained after 120 hours at 200° C. Reduction of the heating temperature to 150° C. produced only diffuse UO_2 x-ray patterns after 720 hours; a preparation heated 120 hours at 177° C. also produced only UO_2 . These results would appear to set 200° C. as

the lower limit for the preparation of coffinite by our procedure. However, coffinite was formed when a standard preparation was heated 120 hours at 120° C. then heated an additional 120 hours at 225° C. This result seems to conflict with that obtained by precipitating the uranium (IV) hydroxide separately and suggests that uranium dioxide can, under proper conditions, be converted to coffinite. If, however, the UO_2 crystallization in the 150° and 177° preparations occurs during the drying step, the formation of coffinite at the lower temperatures becomes strictly a rate problem and the apparent conflict of results is resolved.

A coffinite preparation at 360° C. gave a product with an unidentified x-ray powder pattern. The temperature limits for the formation of coffinite by the conditions outlined are thus 200° C. to <360° C.

Atmosphere of Preparation

Practically all of the tetravalent uranium in a standard preparation heated at 250° C. forms coffinite, as evidenced by the color of the product and the weak-to-absent lines of uranium dioxide in the powder pattern. If the precipitation steps are carried out in air, instead of in an inert atmosphere, a black product results, and the powder pattern shows the presence of a much larger fraction of uranium oxide with the coffinite. The coffinite-uraninite mixture can be partially fractionated by suspension in water. The uraninite settles much more rapidly than coffinite, and the latter can be obtained relatively pure by decanting and centrifuging the suspended material after the bulk of the uranium oxide has settled.

These results indicate that partially oxidized uranium does not take part in the formation of coffinite. Since freshly precipitated $\text{U}(\text{OH})_4$ is very susceptible to oxidation, exposure to the atmosphere must be severely restricted. However, the presence of a reducing agent might permit the preparation of pure coffinite without the necessity of operating in an inert atmosphere. We have not investigated this possibility in detail, as yet.

ANALYSIS OF COFFINITE

One of our coffinite samples analyzed 71.33% UO_2 and 29.20% SiO_2 as compared with a theoretical 81.80% UO_2 and 18.20% SiO_2 for USiO_4 . From this result it is apparent that an 11% excess of silica remained in the coffinite concentrate after the gravity separation. Our best sample, analyzing 24.8% SiO_2 contained only 6.6% excess silica. This sample contained less than 1% moisture after vacuum drying at 70° C. Approximately 75% of this water was removed below 400° C. in a vacuum.

PROPERTIES OF COFFINITE

As differentiated from the black naturally-occurring coffinite, the

synthetic material is a blue microcrystalline solid. A sample of natural coffinite, AE1019 (obtained from Prof. Gruner) turned from black to a grey-green color when ignited to 400° C. in air. The black color appeared to be due, at least in part, to organic matter. The coffinite x-ray pattern was improved as a result of this treatment. Further heating in air to 500° C. however, resulted in a gradual decomposition of the sample to U_3O_8 and SiO_2 .

The structure of synthetic coffinite is tetragonal with $a = 6.981 \pm 0.004$ kX, $c = 6.250 \pm 0.005$ kX. Like natural coffinite, all synthetic material is finely divided as evidenced by the diffuse character of the back reflection lines. No anisotropic crystals can be seen under the microscope. No apparent change in crystallite size was observed when a preparation was heated at 250° C. for as long as 410 hours. Seeding of preparations had no noticeable effect on the size of coffinite crystals, thus emphasizing the necessity for intimate mixing of the constituents to affect crystal formation.

The refractive index of our coffinite dried at 75° C. was 1.83, vacuum ignition to 1000° C. increased this value to 1.88.

INFRARED SPECTRUM

Infrared spectra were obtained of synthetic coffinite as well as of synthetic thorite and natural zircon. Fig. 1 illustrates the similarity of the three orthosilicate spectra.

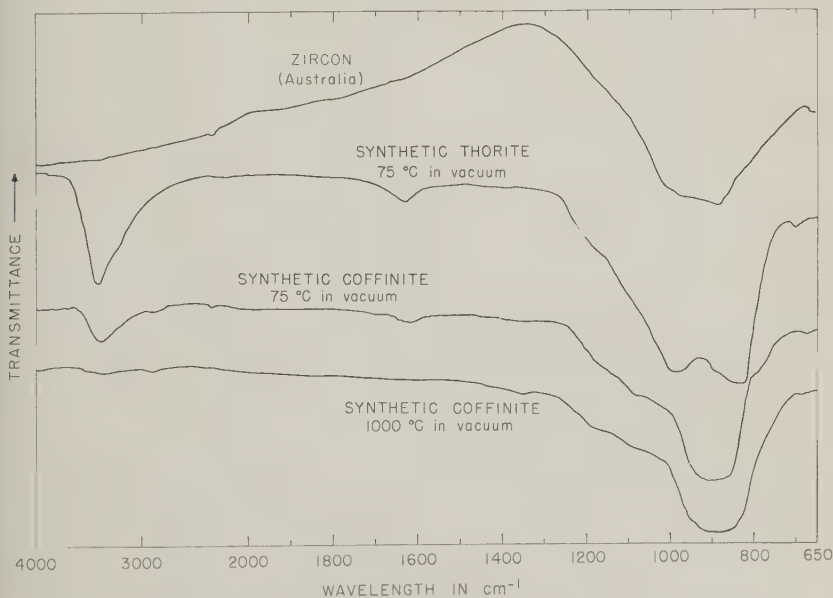


FIG. 1. Infrared spectra of synthetic coffinite, thorite, and natural zircon.

The spectrum of synthetic coffinite vacuum-dried at 75° C. shows moderate O—H absorption in addition to the characteristic isolated SiO_4 tetrahedra absorption reported by Launer (1952) in the region of 11.2 μ . The O—H absorption may be associated with excess silica, coffinite, or both. No rigorous correlation of the frequency of the O—H absorption could be made with other known hydroxyl-containing crystallographic structures. A similar conclusion was reached by Roy and Roy (1957) in their studies on the hydroxyl region of the infrared spectra of brucite, gibbsite and the clay minerals. The spectra of synthetic coffinite showed a steady decrease in the O—H absorption of samples which had been heated in vacuo for several hours at progressively increasing temperatures, until at 1000° C. virtually no trace of the O—H absorption remained. A room temperature x-ray powder photograph of the sample heated to 1000° C. in vacuo showed no change in cell dimension or line intensities compared with the unheated material, which suggests that the synthesized product is USiO_4 without an essential hydroxyl component. Since several per cent of excess silica was present, it seems likely that the water was present as hydrated silica rather than as a hydroxyl-substituted orthosilicate.

THERMAL STABILITY

Synthetic coffinite heated in a vacuum of 10^{-5} mm. Hg for 25 hours at 1000° C. shows no change in its x-ray powder pattern taken at room temperature. Patterns taken at elevated temperatures of a sample sealed in an evacuated vitreous silica capillary show that no phase changes occur during 3 to 4 hour exposures at 200, 400, 600 and 800° C. However, a sample heated in vacuo at 1245° C. for $2\frac{1}{4}$ hours turns brown, the decomposition products are UO_2 and amorphous silica. It is apparent from this observation that coffinite cannot easily be synthesized by a high temperature fusion of UO_2 and SiO_2 . Heating a sample in air at 500° C. for 20 hours results in the fading of the back reflection lines of the powder pattern, and an additional 20 hours at 750° C. produces a U_3O_8 -like pattern with no traces of coffinite lines remaining. The stability limits of USiO_4 are thus placed at 1000° C. in vacuum, and 500° C. in air.

ACKNOWLEDGMENTS

We are indebted to Ralph Telford for the analytical results, and to Elizabeth Sherry and Dr. Stanley Siegel for the x-ray diffraction studies.

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NOTES AND NEWS

UNIVERSAL STAGE ACCESSORY FOR DIRECT DETERMINATION OF THE THREE PRINCIPAL INDICES OF REFRACTION*

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With rare exceptions only two principal indices of refraction of a biaxial crystal can be determined directly on the universal stage by the immersion method, since mechanical limitations prevent rotating all the way to the appropriate position for the third principal index. This usually must be determined by extrapolation from an intermediate index determined at a chosen rotation toward the third position. The extrapolated value, however, is subject to error, for the index at the intermediate position is measured where the change of index per degree of rotation is large. If the universal stage and lens system are not in optimum adjustment, the "corrected optical rotation" of the mineral grain and in turn the extrapolated value of the third principal index are erroneous.

A simple expedient enabling direct determination of all three indices on a single grain consists of mounting the grain on a spindle placed between the universal stage hemispheres in a slotted metal plate of the same thickness as the spindle (Fig. 1). Basically this accessory is a skeletal version of the convenient rotation device for flat stage work suggested by Rosenfield (1950) and elaborated by Wilcox (in press), and when combined with the universal stage, it enables direct angular measurements of certain additional optical and crystallographic elements of the grain, serving the purpose of the pin axis in the complex and little-used Lindley microscope-refractometer (Scheumann, 1931; Fisher, 1931; Winchell, 1937, p. 238). The mineral grain is oriented by the conventional universal stage procedure to permit determination of the first and second principal indices of refraction. Then a rotation of approximately 90° about the spindle axis places the grain in such a position that, with slight refinement of the orientation by the universal stage, the third principal index may be measured. A less desirable alternative would be to set the spindle by cut-and-try in such a position that all three optical symmetry axes may be oriented by suitably steep inclinations on the universal stage axes. These procedures apply likewise in orientating a uniaxial crystal grain.

The optic plane may be brought into a position most favorable for direct measurement of $2V$, and likewise various crystallographic elements may be oriented by suitable manipulation on the spindle axis. Whereas the universal stage alone can bring crystal directions into the orthoscopic

* Publication authorized by the Director, U. S. Geological Survey.

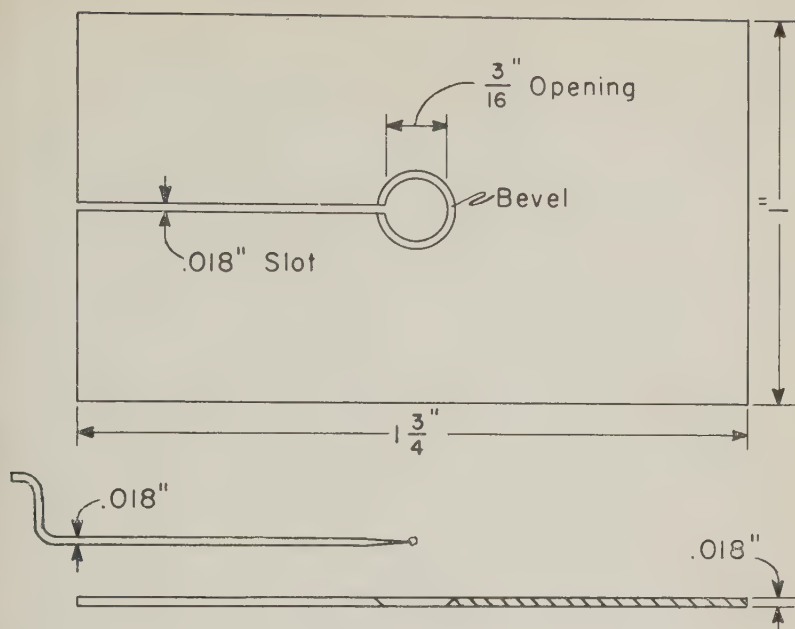


FIG. 1. Metal plate and spindle for grain mount on universal stage.

observation direction from within a cone having an apex angle of about 100° , the addition of the spindle, in effect, sweeps this 100-degree "cone-of-observation" through a full 360° , leaving a "cone-of-blindness" of only some 80° around the spindle axis. This simple device therefore greatly increases the ability to determine the geometric relations between the optical indicatrix and the crystallographic elements of a given grain. In addition it provides a means for holding the grain securely without strain during the measurements and, if desired, for relating the optical characteristics to x -ray results.

In Fig. 1 the spindle is a fine sewing needle measuring 0.018-inch diameter, from the eye-end of which the temper is removed to permit bending in the L-shape. The point of the needle is dulled on a whetstone to prevent creeping of the liquid adhesive and to give a flat surface to press against the grain during mounting. The plate here is made of stainless steel 0.018 inch thick, and a central hole $\frac{1}{8}$ to $\frac{3}{16}$ inch diameter is beveled as shown to minimize reflections. A slot the width of the spindle or very slightly larger is cut through one half of the plate along the long axis.

The procedure for mounting the grain is essentially that described by the writer (Wilcox, in press) for the conventional spindle stage. A mineral

grain somewhat smaller than the diameter of the spindle, say between 0.03 and 0.3 mm. diameter, is chosen for mounting. A drop of adhesive (such as carpenters' glue and molasses) is smeared on a surface and the point of the spindle barely touched to it, after which the point is touched to the desired grain under the binocular microscope. The slotted metal plate is placed directly on the water cell of the 5-axis universal stage over a drop or two of the chosen immersion liquid, and the spindle is placed in the slot with the L-arm flat. (Should the spindle fit too loosely, a bit of the adhesive in the slot provides sufficient firmness.) Immediately after adding another drop or two of the immersion liquid at the beveled hole, the upper hemisphere is set in place, taking care to avoid trapping bubbles in the hole of the metal plate.

The grain on the spindle point is then centered by shifting the metal plate, and if necessary, adjusting its position vertically in respect to the U-stage axes. Starting with the L-arm of the spindle flat, an optic symmetry axis is brought parallel to the microscope axis by the usual universal stage procedure (Emmons, 1943, p. 23 ff), in which position two of the principal indices are measured at their respective extinctions. The spindle arm is then turned to an upright position and the grain is again oriented to bring another optical symmetry axis parallel to the microscope axis, in which position the third principal index may be measured at its extinction. Direct measurement of optic angle is best made, of course, at a spindle setting requiring least tilting of the inner vertical axis of the universal stage, as are also the measurements of relation of crystallographic elements to the indicatrix. The latter data may be plotted in the usual manner on a stereographic net for a given setting of the spindle. For different spindle settings, crystallographic elements can be plotted in respect to each other by reference to the indicatrix at each setting and the "zero azimuth" of the spindle on the inner stage.

Several variations are possible in the basic form of this accessory, depending upon the measurements to be made and on the design of the particular universal stage on which it is to be used. The form sketched in Fig. 1 has been used successfully for indicatrix and crystallographic measurements with the Leitz 4- and 5-axis universal stages by the writer and for index determinations with the Bausch and Lomb 5-axis stage fitted for the double-variation method of refractive index determination by students of Professors R. C. Emmons, R. M. Gates, and S. W. Bailey at the University of Wisconsin, to whom the writer is indebted for suggestions. For accuracy of angular measurements, it is necessary of course that the thickness of the accessory plate should be near that for which the hemisphere assembly was designed (see Piller 1957). Economy of

immersion liquid and convenience in changing liquids may be improved by decreasing the area of the plate, and for an extended series of index measurements, the slotted plate may be cemented in a centered position on the water cell. For measurements on universal stages without water cell, the slotted plate may be cemented to a glass slide to provide the proper total thickness of the mount between hemispheres.

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THE SYMMETRY OF THE COMPLETE TWIN

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In a recent paper (Curien & Le Corre, 1958, to be referred to as CLC) it was shown how the symbolism of the (black-white) Shubnikov groups can be used to designate the various twin laws, in the case of twinning by merohedry or by reticular merohedry.

Every such *twin law* gives the geometrical relationship between two crystals, a "black" one and a "white" one. It may usually be expressed by any one of several possible *twin operations*, which (as is well known) are all the symmetry operations that are deficient in the merohedral crystal symmetry but are present in the next-higher merohedry. If the crystal symmetry is a hemihedry, say $4/m$, only one twin law is possible: the next-higher merohedry, in this case, is the holohedry $4/m\ 2/m\ 2/m$, and the twin operation may be chosen at will from four 180° rotations or four reflections; the corresponding *twin elements* are primed in the *twin*

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symbol $4/m\ 2'/m'\ 2'/m'$. Another hemihedry, say $4\ 2\ 2$, gives another twin law, with the symbol $4/m'\ 2/m'\ 2/m'$ (as written by CLC); the *twin center* need not be explicitly denoted by $\bar{1}'$, to stress the fact that inversion too is a possible twin operation, because $2/m'$ implies $\bar{1}'$. In the case of a tetartohedry, there will be as many possible twin laws as there are hemihedries that have the given tetartohedry as a subgroup. Example: the polar tetartohedry 4 leads to three twin laws: $4/m'$, $4\ 2'\ 2'$, and $4\ m'\ m'$. Finally the ogdohedry 3 gives seven twin laws (listed by CLC, *loc. cit.*, Table I).

The concept of *twin symmetry* or *symmetry of the complete twin*, recently revived by M. J. Buerger (1954), was already discussed by G. Friedel (1904; 1926). In twinning by merohedry or by reticular merohedry, the *complete twin* is defined in each case as the edifice that comprises, in addition to an original crystal, as many twinned crystals as there are possible twin laws. In the case of low-temperature quartz, of symmetry $3\ 2$, the four individual crystals¹ are shown by CLC (*loc. cit.*, Fig. 1),² with an indication of the twin law that holds for any two crystals: $6'\ 2\ 2'$ for I-II and III-IV, $6'\ 2\ m'$ for I-III and II-IV, $\bar{3}'\ 2/m'$ for I-IV and II-III. The notation of the black-white groups also brings out the fact that the product of any two of these three twin laws is equal to the third one.

By an immediate generalization the notation can be made to express the symmetry of the complete twin. Let each of the four crystals I to IV have its own color; let the twin operations that bring I to coincidence with II, III, and IV be designated, respectively, by the signs prime, double prime, and triple prime attached to the corresponding twin elements. The twin symmetry receives the symbol $6'/m''\ 2/m''' \ 2'/m''$. The crystal-symmetry elements are unprimed; the twin axes of the Dauphiné law are primed ($6'$ implies $2'$ and 3); the twin planes of the Brazil law are double-primed; the product of the two laws is shown by triple primes attached to the twin center (both $2/m'''$ and $2'/m''$ imply $\bar{1}'''$) and twin planes (mirrors of the first kind of the lattice).

It may also be remarked that, in the most complicated case, that of twinning by ogdohedry, the notation can be simplified. Only one kind of prime sign is needed ($6'/m'\ 2'/m'\ 2'/m'\ \bar{1}'$) as every primed element stands for a different twin law. Note that, in this case, it is advisable to symbolize the twin center explicitly, so that all seven twin laws are shown in the symbol.

Let us now consider a species that can twin both by merohedry and by reticular merohedry; for instance, dolomite, of symmetry $\bar{3}$ (CLC, p.

¹ Often called *individuals* for short.

² Note that, in order to comply with the convention current in U.S.A., Fig. 1 of CLC should be rotated in its own place 30° counter-clockwise.

128-9; Fig. 2).³ Only one twin law exists in twinning by merohedry; it is correctly written $\bar{3} 2'/m'$, a symbol that expresses both the twin law and the symmetry of the twin. The two additional twin laws that are made possible by reticular merohedry, $\bar{3} 1 2''/m''$ and $6'''/m'''$, will lead to the complete twin, comprising four crystals in all, the symmetry of which is written $6'''/m''' 2'/m' 2''/m''$, in which $6'''$ implies $2'''$ so that $6'''/m'''$ implies $\bar{3}$. We note that this symbol would apply equally well if the crystal had an hexagonal lattice and all twin laws were due to merohedry.

How does the generalized notation work in the case of cubic crystals? Consider a twin by hemihedry, with crystal symmetry $4 3 2$. The twin law is denoted by $4/m' \bar{3}' 2/m'$ (CLC, Table I), a symbol which also expresses the symmetry of the twin. A crystal that belongs to the tetartohedry, $2 3$, can have three twin laws: $2/m' \bar{3}'$, $4'' 3 2''$, $\bar{4}''' 3 m'''$ (symbolized by CLC); the complete twin comprises four crystals. The task of symbolizing the complete twin symmetry is here complicated by the fact that we are trying to represent a *symmetry operation* by a symbol that denotes either a set of equivalent symmetry elements or at least one symmetry element. (A *symmetry element* is a cyclic group, standing for all the powers of the operation.) The *twin operation* in the twin law $4'' 3 2''$, is a 180° rotation about any one of the six 2-fold axes of the lattice or a $\pm 90^\circ$ rotation about any one of its three 4-fold axes. CLC have circumvented the difficulty for one twin law at a time by pointing out that $4''$ implies 2 ($4'' \supset 2$). To be more explicit we would have to write the symbol as $4''[\supset 2] 3 2''$. Likewise $\bar{4}''' 3 m'''$, or $\bar{4}'''[\supset 2] 3 m'''$, should serve as a reminder that the twin operation is a reflection in any one of the six mirrors of the lattice or a $\pm 90^\circ$ rotatory-inversion about any one of its three $\bar{4}$ -axes. Again the CLC symbol $2/m' \bar{3}'$ immediately indicates that the twin operation is the inversion through the symmetry center of the lattice or a reflection in any one of its three mirrors; although not so obvious from the symbol, other possible twin operations are $\pm 120^\circ$ rotatory-inversions about the four $\bar{3}$ -axes of the lattice.

The symbol for the symmetry of the complete twin, in its expanded form,

$$\frac{4''}{m'} \supset [\bar{4}'''] [\supset 2] 3 \frac{2''}{m''} \bar{1}',$$

will look somewhat cumbersome. The abbreviated symbol, $m' 3 m'''$, which implies $2''$, is probably more convenient; each twin law is defined by an operation of order 2, namely a reflection or a 180° rotation.

³ To comply with current American convention, Fig. 2 of CLC should be rotated 180° in its own plane, so that a face of the rhombohedron will slope toward the observer.

From the group-theory viewpoint,⁴ a twin is a *representation* of an abstract *factor group* (C_2 , $S_{2 \times 2}$, $S_{2 \times 2 \times 2}$ in twinning by hemihedry, tetartohedry, ogdohedry, respectively). In the above example the 48 symmetry operations of the holohedral point group $m\ 3\ m$ are divided into one subgroup and three cosets; the operations of the *subgroup* describe the crystal symmetry $2\ 3$, those in each *coset* are all the possible twin operations for one of the three twin laws. The factor group is a four-color group that differs in structure from the four-color space groups described by Belov and Tarkhova (1956). In our example all the elements of the factor group that correspond to changes of color are of order 2 ("element" being given its group-theory meaning, corresponding to "operation" in crystallographic groups); in the four-color space groups studied by Belov and Tarkhova, the factor group is the cyclic group C_4 .

We wish to thank Professor J. Wyart and Dr. Gabrielle Donnay for a critical reading of the manuscript.

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⁴ To readers unfamiliar with the subject of groups, we take pleasure in recommending Bryan Higman's "Applied group-theoretic and matrix methods" (Oxford, 1955). We have found this book illuminating, although we must say that not all its statements about crystals can be taken at face value. Mineralogists and crystallographers will not agree that the study of the external forms of crystals is "metaphorically, as well as literally, superficial" (p. 90); they will not be easily persuaded that the five trigonal point groups are possible only with a rhombohedral lattice (p. 110), nor will they see why the space groups of $4\ 2\ m$ are distributed among *four* lattice modes (p. 132) when only *two* are possible (p. 121)!

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NOTE ON "REVOREDITE" AND RELATED LEAD-SULFUR-ARSENIC GLASSES*

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Recently Amstutz, Ramdohr, and de las Casas (1957) have described as a new mineral, "revoredite," from Cerro de Pasco, Peru, which is

* Publication authorized by the Director, U. S. Geological Survey.

"amorphous to x-rays" and consists essentially of lead, arsenic, and sulfur. We have studied another material "amorphous to x-rays," from Quiruvilca, Peru, also consisting essentially of lead, arsenic, and sulfur, in different proportions, however. We find that a probably continuous series of amorphous phases can be made in the compositional range from As_2S_3 to $2\text{As}_2\text{S}_3 \cdot \text{PbS}$ and probably in still more lead-rich parts of the join $\text{PbS}-\text{As}_2\text{S}_3$. "Revoredite" falls within this range; the Quiruvilca material ($\text{As}_2\text{S}_3 \cdot 2\text{PbS}$) is beyond it, but its properties are so similar to those of the synthetic glasses that no break in the series between As_2S_3 and $\text{As}_2\text{S}_3 \cdot 2\text{PbS}$ seems likely. The question is raised whether any particular composition in such a series of uncrystallized solids, virtually lead-arsenic-sulfur glasses, should be recognized as a mineral species or given a name, such as "revoredite." Certainly, we are not proposing a name for the Quiruvilca material; but will refer to it here as "the Quiruvilca lead-arsenic-sulfur glass," or briefly, the Quiruvilca material.

Its history is as follows. In 1952 Mr. Lawson P. Entwistle, Chief Geologist, Northern Peru Mining Corporation, Lima, Peru, called the attention of Mr. Frank S. Simons of the U. S. Geological Survey to an unusual ore specimen taken from the Sin Nombre vein of the Quiruvilca Mine, La Libertad Department, Peru. The specimen was essentially massive brown sphalerite with galena and pyrite, but had a dark-gray botryoidal coating whose appearance is shown in Figs. 1*a*, *b*. The underlying massive sulfide ore and structure of the amorphous material are shown in Figs. 2 and 3.

In a letter dated October 1, 1953, Mr. Simons gave further data concerning the specimens. "The mineral is very scarce in the mine . . . The specimens come from the 50 level of the Sin Nombre vein, about 250 meters below the surface, from a large vug about 5 meters long in a vein slightly less than one meter wide. The vein consists of approximately 70% pyrite, 22% wurtzite (?), 6% galena, 2% tetrahedrite, and a little chalcopryrite. Gangue is quartz and is not abundant. Sulfide sequence of deposition is galena (oldest), wurtzite, pyrite, tetrahedrite and chalcopryrite; wurtzite veins pyrite; pyrite does not seem to replace anything; tetrahedrite replaces galena and wurtzite; tetrahedrite is associated with chalcopryrite and the two are probably essentially simultaneous. This section of the vein lies in the transition zone between enargite-pyrite veins in the center and lead zinc veins outside . . ." Later work in Washington indicated that the wurtzite (?) is mostly or all sphalerite.

An x-ray diffraction study by Joseph M. Axelrod of carefully separated material from the coating showed it to be "amorphous to x-rays." Chemical tests showed much lead and arsenic.

A chemical analysis is given in Table 1, analysis (*a*) and, for comparison, two published analyses of "revoredite," and one of "natural sulfide

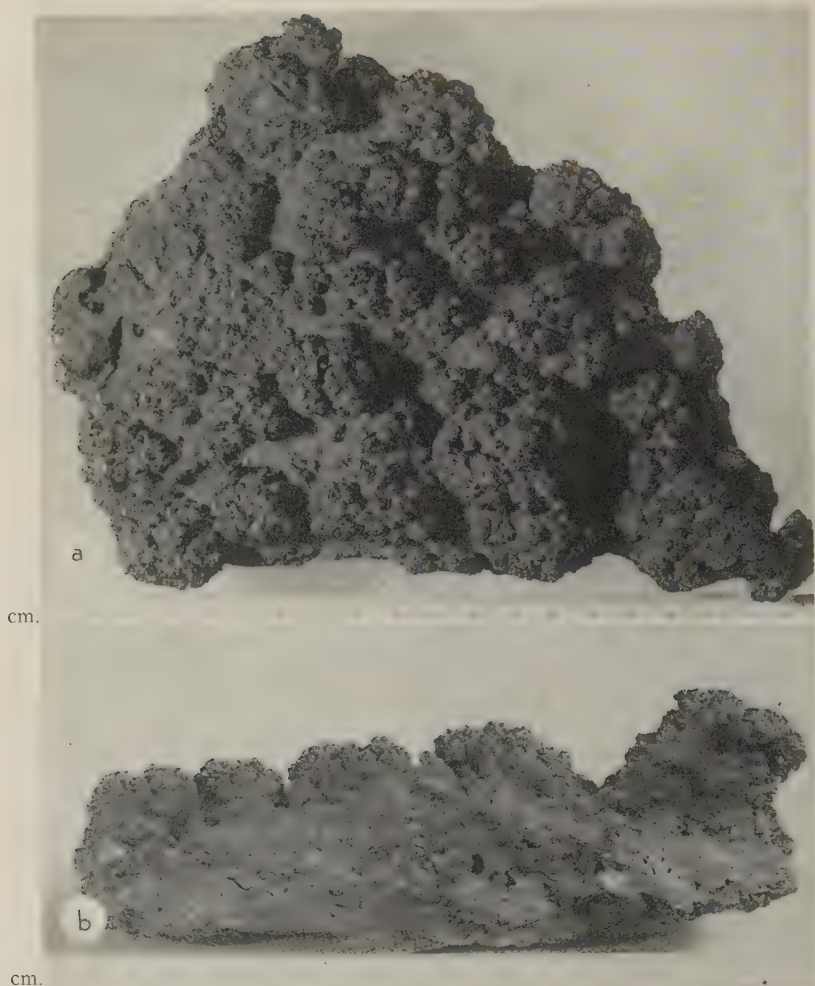


FIG. 1. Massive sphalerite-galena ore coated with botryoidal lead sulfarsenide glass, from Quiruvilca, Peru.

(a) View of top showing continuous coating.

(b) Side view of broken specimen, showing massive ore with top coating of glass.

glass," also from Cerro de Pasco. Both "revoredite" and the "glass" have been recently described, by Amstutz, Ramdohr, and de las Casas (1957), and Amstutz (1958), respectively. Presumably "revoredite" and the "glass" are the same, the difference in analyses notwithstanding; and it may be noted that the name "revoredite" is not used by Amstutz in his later paper.*

* In a letter to C. M. (of date May 3, 1959) Amstutz states that the "Revoredite"

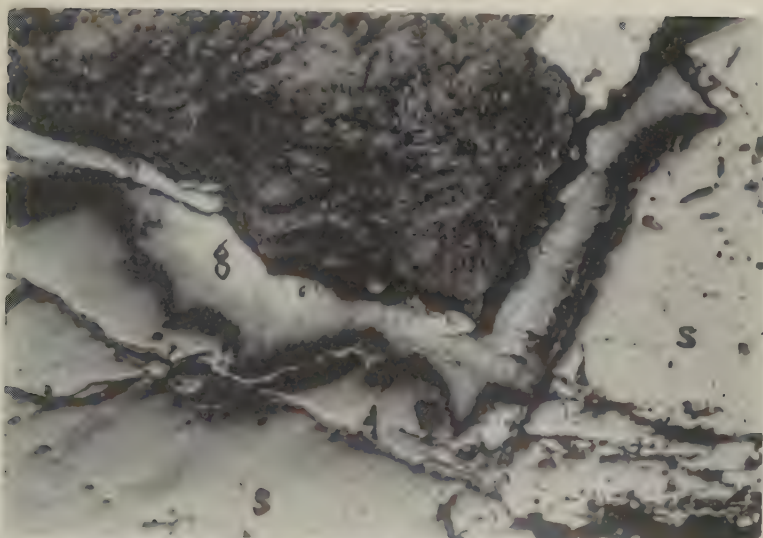


FIG. 2. Polished section ($\times 110$) of sphalerite (s) with continuous rim (g) of lead sulfarsenide glass.

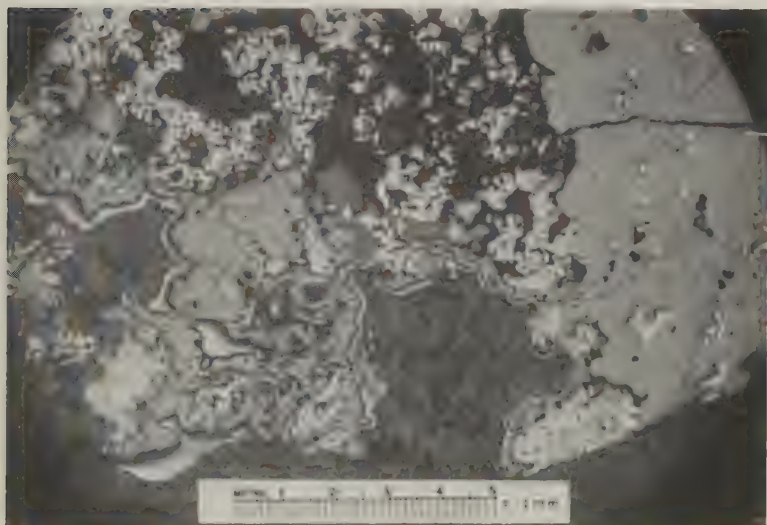


FIG. 3. Polished section of sphalerite (gray), galena (white) and lead sulfarsenide glass (continuous rim, light gray).

analyses "were made by a commercial lab . . . which was unfortunately not able and equipped for such . . . work. The natural sulfide glass analyses however are in 3 analyses of 3 samples from different places of one stope . . . all extremely close (only about .1 difference)."

TABLE 1. ANALYSES OF THE QUIRUVILCA MATERIAL, OF "REVOREDITE," AND OF "NATURAL SULFIDE GLASS"

	Quiruvilca material ¹ (Analyst, Blanche Ingram) (a)	2PbS·As ₂ S ₃ (Theoretical) (b)	"Revoredite" Cerro de Pasco (Amstutz, Ramdohr, and de las Casas, 1957) (c) (d)		"Natural sulfide glass" Cerro de Pasco (Amstutz, 1958) (e)
As	18.4	20.7	52.1	51.9	23.10 ± .70
Sb	1.7	—	—	—	—
Pb	55.6	57.2	8.7	2.7	20.55 ± .45
Cd	0.7	—	—	—	—
Zn	1.1	—	—	—	—
S	22.4	22.1	34.9	34.9	56.35 ± .25
Tl	—	—	0.5-1.0	0.5-1.0	.04
	99.9	100.0			

¹ Semiquantitative spectrographic analysis by Katherine V. Hazel, U. S. Geological Survey, showed the following trace elements: Sb 1.0, Cd 1.0, Zn 0.3, Ca 0.01, Cu 0.01, In 0.03, Fe 0.003, Mg 0.003, Al <0.001, Ag 0.0003, Ba 0.0003, Bi 0.003, Si 0.0003. Figures are reported to the nearest number in the series 1.0, 0.3, 0.1, 0.03, 0.01, 0.003, etc., in per cent. These numbers represent midpoints of group data on a geometric scale. Comparisons of this type of semiquantitative results with data obtained by quantitative methods, either chemical or spectrographic, show that the assigned group includes the quantitative value about 80 per cent of the time. Thallium, if present at all, is less than 0.01 per cent in the Quiruvilca material.

For the analysis of the Quiruvilca lead-arsenic-sulfur glass, 175 milligrams of carefully hand picked (under the microscope) material was used. Any particle showing galena or sphalerite was rejected.

For the arsenic determination, about 50 milligrams of sample was decomposed with HNO₃. Lead sulfate and elemental sulfur precipitated on decomposition. The sulfur was brought into solution by prolonged digestion with HNO₃. The HNO₃ was evaporated and arsenic was separated from the other constituents of the sample by distillation from a hydrochloric acid medium at 110° C. The acidity of the distillate was adjusted to 9 N and the distillate was treated with H₂S. Arsenic was precipitated and weighed as As₂S₃.

Antimony was determined colorimetrically as iodoantimonous acid. A 50-mg sample was decomposed with HNO₃. Tartaric acid was added to lessen chances of coprecipitation of Sb with PbSO₄. The nitric acid was evaporated with PbSO₄ filtered off. The filtrate was used for color development. The other elements, in amounts present, do not interfere in the colorimetric method.

Lead was determined gravimetrically as PbSO₄. Sample size was approximately 50 mg.

An aliquot of the filtrate from the lead determination was used for the cadmium determination. Cadmium was precipitated and weighed as cadmium thiourea reineckate. A separation of Cd and Zn is not necessary in this procedure.

Zinc was determined colorimetrically with zincon reagent on an aliquot of the filtrate

from the lead determination. Zn was separated from Cd by use of ion exchange resin Dowex—1×8. Cadmium and zinc were absorbed from a 2 M HCl solution. Zinc was eluted with 0.01 M HCl.

Sulfur was determined gravimetrically as BaSO_4 . A 25-mg. sample was fused with $\text{Na}_2\text{CO}_3\text{-KNO}_3$. The fusion mixture was leached with H_2O . The water solution was used for the analysis.

Our colleague, Priestley Toulmin, III, prepared for us lead-arsenic-sulfur glasses of molar compositions $3.95\text{As}_2\text{S}_3\cdot\text{PbS}$ and $2.00\text{As}_2\text{S}_3\cdot\text{PbS}$ by fusing at $1100^\circ \pm 10^\circ \text{C.}$, a mixture of synthetic As_2S_3 glass and crystalline PbS in sealed evacuated silica glass tubes, and quenching in water.

As to the genesis of the natural glasses, the microscopic evidence indicates that a sphalerite with galena inclusions (this relation points to earlier events in the history of the ore with which we are not now concerned) came in contact with vapors or solutions with varying lead content and rich in arsenic trisulfide, whereby stalactitic crusts such as "revoredite," or a glass of the Quiruvilca type with composition close to dufrenoyite were formed. The possibility of a mine fire being involved in the formation of these substances has been considered; but there is no record of any fire in these workings.

Amstutz, Ramdohr, and de las Casas (1957, p. 30) observe that amorphous lead sulfarsenides similar to "revoredite" have been found in Wiesloch, Baden, Germany. Ramdohr's (1955) description of jordanite from that locality is of interest, "... concentric spheroidal to botryoidal masses, often forming crusts on sphalerite, with clearly marked former gel-structure, now coarsely crystallized in roughly parallel crystals." Presumably the crystallized and the amorphous lead sulfarsenide have a similar origin. The "colloidal" character of synthetic arsenic trisulfide is familiar to all analytical chemists. That a lead sulfarsenide composition such as dufrenoyite may have a colloidal or glassy state is not so well known. Concerning these substances, Pascal (1933) observes, "The physical chemistry of these substances does not appear to have been studied. Other than purely mineralogical studies on this group, there is only the work of Sommerlad who attempted the synthesis of some of these minerals." Sommerlad (1898) melted together PbS and As_2S_3 and obtained a lustrous black, brittle mass of specific gravity 4.585, which was shown by analysis to have the composition $\text{PbS}\cdot\text{As}_2\text{S}_3$ (sartorite). The specific gravity of the natural mineral is considerably higher (5.05) and Sommerlad may have had a glass. On moderately heating this material in a current of hydrogen sulfide, As_2S_3 was formed, and the dark gray residue had the composition and specific gravity of dufrenoyite, $2\text{PbS}\cdot\text{As}_2\text{S}_3$. Further heating until no more As_2S_3 formed, left a dark-gray substance with the composition of jordanite, $4\text{PbS}\cdot\text{As}_2\text{S}_3$. Dufrenoyite, or a crys-

talline mass of that composition and specific gravity, was also made by fusing 2PbS and As_2S_3 at a moderate temperature.

The name "revoredite" proposed by Amstutz, Ramdohr, and de las Casas appears untenable for the very reason that these authors propose for its acceptance. "The name Revoredite . . . was proposed . . . in case that a crystalline sample should be found, or that by some method, it might be possible to attribute a crystalline structure to this so far amorphous mineral." If crystalline phases do appear, they will simply be orpiment or one or more of the series of sartorite-dufrenoy-site-jordanite.

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MINERAL SEPARATION WITH ASYMMETRIC VIBRATORS

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INTRODUCTION

Geochemical studies often require the separation of gram amounts of pure minerals from rocks. Hand picking is usually out of the question and one resorts to such well-known techniques as heavy liquid separation with bromoform, tetrabromoethane, or methylene iodide (Fairbairn, this journal, 1955), magnetic separation, (*ibid.* and Gaudin and Spedden, 1943; McAndrew, 1957; Rosenblum, 1958; Rubinstein *et al.*, 1958) or to laboratory adaptation of industrial beneficiation processes like flotation or the Wilfley table. Many other techniques are used for particular problems: sieving, panning, various arrangements for elutriation with air or

water, not to mention the old trick of shaking grains on a sheet of paper to recover flakes of mica.

While separating minerals for geologic age determination, we have evolved a number of special ways to facilitate the recovery of various minerals, particularly zircon, biotite and muscovite. Several of our devices are based on the industrially well-known principle of asymmetric vibration.

THE ASYMMETRIC VIBRATOR

When a particle is placed on a smooth horizontal plane and the plane is made to vibrate horizontally or vertically, the particle will either slide to and fro or hop up and down, but will remain essentially on the

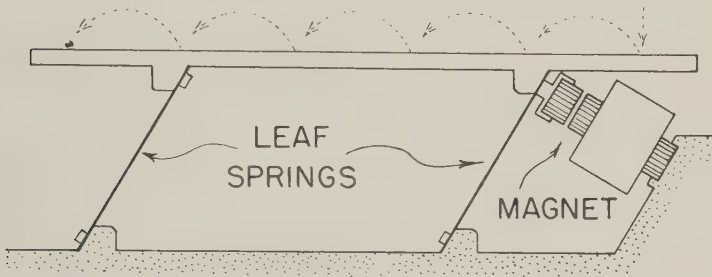


FIG. 1. The asymmetric vibrator and the motion of a particle upon it.

same spot. However, if the plane is made to vibrate sinusoidally in any other direction, the grain will take off and march in a series of hops in the direction of the smallest angle between the plane and the direction of the vibration. We illustrate this motion, as nearly as it can be illustrated, in Fig. 1. An electromagnet (in practice a dismantled filter choke) supplies the energy for the vibration. The rate of advance depends on the length of the hops made by the particles. This is a function of the amplitude of vibration, which in turn is determined by the voltage impressed on the magnet. In this way, a rheostat or a variable transformer serves as a continuous control of the rate of feed. Sixty-cycle alternating current produces a vibration frequency of 120 cycles/sec. because the magnet gives two mechanical strokes for each cycle received. With a half-wave rectifier in the circuit, the second stroke for each cycle can be eliminated and a mechanical vibration of 60 cycles/sec. produced. As a rule one tries to drive these vibrators at about the resonant frequency of the system, but we have found that this requirement is not too stringent. The resonant frequency is, of course, adjustable

by controlling the strength of the blade springs that support the vibrating plate.

The angle of these springs with the plane is usually about 60° , and the drive is perpendicular to them, giving an angle of 30° between the plane and the direction of vibration. Again, this angle is not critical; we have used angles from 10° to 45° on vibrators for various purposes.

The linear hopping motion can be turned into a circle (or, more accurately, a spiral) by making the plate circular and mounting it on three or four inclined leaf springs radially arranged in positions symmetrical about the center of the plate. The magnet is mounted in the center, driving in the vertical direction. Industrial mechanical parts feeders use this modification of the asymmetric vibration principle. In mineralogy, small models of these parts feeders have been adapted to various tasks of picking and sorting.

FEEDERS

Even though the pure end product of a mineral separation may be only a gram or less, one may have to feed tens of kilos of a powder through a device to obtain the final result. In most applications, this feed should be uniform and have a continuously adjustable rate. Industrial feeders based on the asymmetric vibration principle are widely used for such diverse applications as loading coal and salting potato chips. Small industrial feeders are available (one make is illustrated by Fairbairn, 1955) and are useful for feeding Wilfley tables, flotation cells, disc-type magnetic separators, and sieving machines. However, they are too large for feeding the paramagnetic ("Isodynamic") separator or the mica separator described further on.

For some of these applications a very slow feed is desired, almost a grain at a time, and we have developed a special feeder for the purpose. This device consists of a small 24-volt D. C. relay with the points soldered in the open position and an aluminum cradle bolted to the relay anchor. A bent glass hopper-funnel is attached to the cradle by small coil springs (Fig. 2). When the relay is energized with low-voltage 60-cycle alternating current from a rheostat or a small variable transformer, the funnel vibrates at a frequency of 120 cycles/sec. with amplitude proportional to the voltage. With a half-wave selenium rectifier in the circuit, the vibration will have a frequency of 60 cycles/sec., which may be advantageous for materials that tend to "hang up" at the higher frequency. A hopper with a volume of about 10–20 cc. and an orifice about 3 mm. in diameter will feed 40-mesh (0.4 mm.) material very nicely with 10–30 volts AC on the coil. Smaller orifices are advantageous for slow feeding of finer powders.

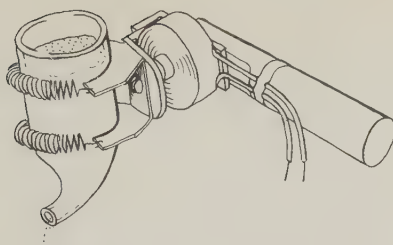


FIG. 2. Slow power feeder made with a d-c relay and a glass hopper-funnel. For clarity, only the essential parts of the relay are shown. The hopper holds about 25 cc.

An ordinary laboratory funnel can be used to feed the small vibrating hopper. There is no limit on the size of this larger funnel, as long as the funnel orifice is drawn down to a size that will not interfere with the motion of the powder in the hopper. This arrangement permits slow, continuous feeding of the Isodynamic separator overnight, for example.

PARAMAGNETIC SEPARATION

The "Isodynamic" separators widely used in geochemical laboratories sort paramagnetic minerals by their magnetic susceptibility. Ferromagnetic particles seek the nearest pole, but a paramagnetic grain in a divergent magnetic field will seek the region of highest magnetic flux concentration between the poles. If the resultant force is now balanced against the force of gravity, separations can be made between minerals of different magnetic susceptibilities.

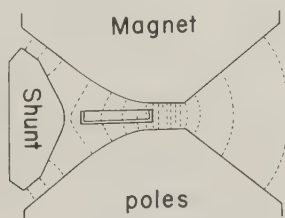


FIG. 3. Schematic transverse section through the magnetic field of a paramagnetic separator. The sample passes down the trough which is placed in the region of widest uniform divergence of flux line density.

A divergent magnetic field is produced between suitably shaped pole pieces (Fig. 3) and the divergence can be further increased by a properly shaped magnetic shunt. The commercially available paramagnetic separators introduce the particles into the region of greatest field divergence by sliding them along a longitudinally vibrating inclined plane. The slope of this plane is also adjustable at right angles to its inclination.

The more strongly paramagnetic grains are pulled up into the higher magnetic field as they slide and a septum prevents them from falling back into the main stream as they leave the magnet. Apart from the noise that these vibrators make, the system has the obvious disadvantage of continuous contact between the grains and the plane they slide on. The resulting differential effects of friction and mutual interaction of the grains tend to reduce the sensitivity of separation in many instances.

These difficulties can be overcome with the asymmetric vibrator. Fig. 4 shows a commercial paramagnetic separator modified with an asymmetrically vibrating trough to transport the grains through the magnetic field. The grains hop along the trough and are acted upon by the field while they are in the air, without much regard to their shape, size, or surface texture. Mutual grain interaction is also minimized by the hopping motion. As illustrated, the paramagnetic separator is usually oper-

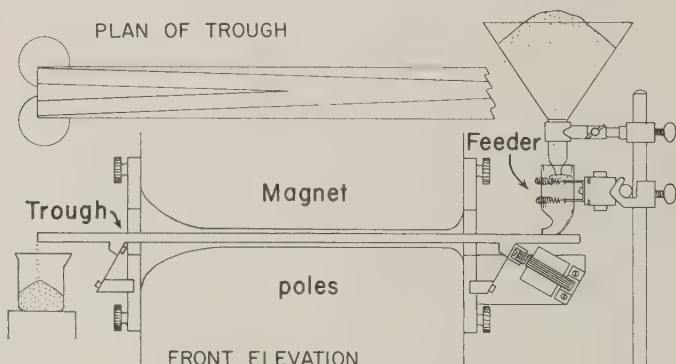


FIG. 4. Asymmetrically vibrating trough with the slow powder feeder (See Fig. 3) mounted on an "Isodynamic" separator.

ated in the horizontal position. However, for special separations involving differences in grain size or shape, there may be advantages in using either positive or negative inclination.

Very fine powders (-200) may form clumps when transported in this way. We have successfully separated small quantities of such fine materials by constructing a special trough with high side walls, closed ends, and built-in sloping bottom, and passing the material through the field submerged in a liquid. The hopping motion is damped by the liquid, but the small particles are kept free of each other. One cannot simply state the lower limit of particle size that can be conveniently handled that way. In general, materials of higher density can be handled in finer fractions.

THE MICA SEPARATOR

We have already mentioned the simple procedure for separating mica from other, rounder grains that tend to roll off an inclined plane, leaving the flat grains behind. One may separate a number of minerals in this way, depending on the differences in cleavages.

Our most successful mica separator is an aluminum plate about 10 inches wide, about 12 inches long, and $\frac{1}{4}$ inch thick, mounted on the base of a commercial vibrating feeder. The plate is mounted at a slant of about 15° to one side (Fig. 5) and is made to vibrate asymmetrically

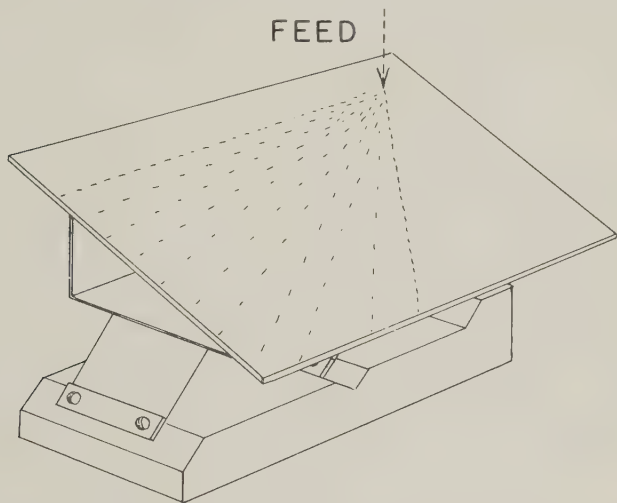


FIG. 5. The inclined-plane mica separator. The smooth aluminum table measures 11×13 inches and slopes 15° . It is mounted on the base of a commercial vibrating feeder.

along its length. The powder is fed to the plate with one of the small shaking feeders we have discussed (Fig. 2). When the amplitude of vibration is adjusted just right for the grain size of the powder, the flattest grains will march lengthwise across the plate and fall off the far end, while the rounder grains bounce and roll down the slope. Troughs around the plate collect the product in a continuous spectrum from the roundest to the flattest and cuts may be made wherever desired. The procedure is rather wasteful, for the thicker books of mica will bounce and roll along with the quartz and feldspar grains. However, such difficult separations as biotite-chlorite, for example, are feasible with this vibrator.

Fairly close sizing tends to increase the efficiency of the separation. The best separation is obtained in the range minus 40 plus 100 mesh.

Working drawings of these devices are available from the authors.

ACKNOWLEDGMENTS

The work outlined in this note is admittedly a side line. We have experimented with these devices from time to time for several years, and many individuals have helped us with valuable suggestions. It is difficult to recall them all by name. We are grateful to M. R. Forrer and M. H. Maeschler of the Institute of Physics, University of Strasbourg, and to Profs. F. Houtermans and E. Niggli of the University of Bern. Faul acknowledges the support of the U. S. Educational Commission for France (Fulbright program) during the early mineral separation experiments in Strasbourg. The assistance of the Syntron Company, Homer City, Pa., and the W. Flämrich Co., Recklinghausen, Germany, is also acknowledged.

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PECTOLITE IN MICA PERIDOTITE, WOODSON COUNTY, KANSAS*

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Pectolite has been identified by optical and x-ray diffraction techniques as a major constituent in the groundmass of one facies of the Hills Pond peridotite, section 32, T. 26 S., R. 15 E., Woodson County, Kansas. The occurrence of pectolite as a major component of the groundmass of a facies of peridotite seemingly is unique. Pectolite has been recognized as a secondary mineral in cavities and seams in mafic eruptive rocks as at Weehawken and Patterson, New Jersey, and as a minor component in syenitic rocks as at Hot Springs, Arkansas and in the Kola Peninsula, U.S.S.R. (Dana and Ford, 1932, p. 567). Some pectolite has been found

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where serpentinized ultramafic rocks have been intruded by younger, less mafic rocks (Bloxam, 1954, p. 527; Parsons, 1924, p. 55-57). Further, pectolite has been reported in South African kimberlite (Mountain, 1931, p. 70-74) as encrustation on less mafic foreign inclusions, on slickenside surfaces bounding the kimberlite pipes, and locally as isolated spheres and tufts in the kimberlite.

The Hills Pond peridotite has been mapped by Wagner (1954). It crops out in the center of a gentle dome and is bounded on the north by a fault. Sills of the peridotite finger from the main body of peridotite along the fault southward into Pennsylvanian shale, limestone, and sandstone. Thin-section studies of samples of the peridotite taken from both the outcrop and diamond-drill core show that, in most places, the rock is a serpentinized mica peridotite containing about 25 per cent phlogopite and less than 10 per cent each of olivine remnants, diopsidic augite, and pleochroic, light-red-brown amphibole as phenocrysts in the serpentine groundmass. Minor constituents include apatite, magnetite, and perovskite. Locally in the subsurface, the rock has a groundmass that is composed almost completely of fine-grained phlogopite and contains phenocrysts of the major constituents given above. At the surface, the serpentine groundmass has weathered in large part to nontronite (?), and the phlogopite has weathered to a mixed-layer vermiculite mineral.

The pectolite was found in a thin-section of peridotite core samples from a sill that is at least 30 feet thick and whose top is at a depth of 765 feet. The upper 10 feet of the sill, which intrudes dark-gray Galesburg shale (Pennsylvanian), contains pectolite as a major component of the groundmass. Directly below the pectolitic rock, the sill holds phenocrysts of amphibole, augite, and olivine in a groundmass composed mainly of very fine grained phlogopite. The groundmass of the sill gradually becomes serpentinitic with depth.

The rock containing the pectolite is light gray and speckled with light-brown phlogopite. In thin section it is seen that the rock contains about 40 per cent phlogopite as subhedral books measuring as much as 2 mm. in length and as smaller fragments in the groundmass that measure as little as 0.025 mm. in length. The phlogopite has reversed absorption ($X > Y > Z$) and the books commonly have frayed ends that are intergrown with pectolite in the groundmass. The groundmass includes 1 or 2 per cent perovskite as anhedral patches or blebs as large as 0.1 mm. in diameter. The perovskite grains are surrounded by subcircular patches of a brown, radially fibrous carbonate (dolomite(?)) as much as 0.3 mm. in diameter that is clouded by leucoxene. The patches of dolomite(?) approximate 8 per cent of the rock, and seemingly have replaced other components of the groundmass. Trace amounts of magnetite as anhedral grains measuring less than 0.03 mm. in diameter are scattered through

TABLE 1. *d*-VALUES IN ANGSTROMS OF X-RAY REFLECTIONS FROM PECTOLITE SAMPLES FROM HILLS POND PERIDOTITE, SECTION 32, T. 26 S., R. 15 E., WOODSON COUNTY, KANSAS, AND FROM PATTERSON, NEW JERSEY. DATA OBTAINED USING GENERAL ELECTRIC DEBYE-SCHERER CAMERA (14.32 CM. DIAMETER) AND $\text{CuK}\alpha$ RADIATION

<i>d</i> Å	Relative intensity estimated	<i>d</i> Å	Relative intensity estimated	<i>d</i> Å	Relative intensity estimated
7.82	<1-1	1.94	<1-1	1.35	<1-1
7.02	<1-1	1.92	<1-1	1.29	<1-1
5.50	1	1.88	1	1.28	<1
3.90	3	1.83	1	1.24	<1-1
3.50	2	1.77	<1-1	1.166	<1-1
3.31	5	1.75	3	1.133	<1-1
3.28	2	1.71	3	1.101	<1-1
3.08	6*	1.67	<1-1	1.089	<1-1
2.92	10	1.66	1	1.080	<1
2.74	3	1.60	1	1.062	<1
2.59	3	1.56	<1-1	1.040	<1
2.43	1	1.55	2	0.995	<1-1
2.33	1	1.52	<1-1	0.921	<1
2.31	1	1.49	1	0.884	<1
2.17	3**	1.47	2	0.866	<1
2.09	<1-1	1.39	<1-1	0.852	<1
2.00	1	1.37	1		

* Skewed to 3.15Å.

** Doublet (?)

parts of the groundmass and as inclusions in the phlogopite books. About 3 per cent of the rock is nontronite(?) (identification as a montmorillonite confirmed by x-ray diffraction), which occurs as green patches measuring as much as 2 mm. in length and in which minute, strongly birefringent flakes are discernible. Melilite, which constitutes not more than 1 per cent of the rock, is present in the groundmass as 0.8-mm. patches of squarish uniaxial negative grains and as disseminated individuals measuring 0.01 to 0.25 mm. across. The birefringence (about 0.007) and negative sign indicate that the melilite may have a composition near that of gehlenite. Much of the groundmass (about 20 per cent of the rock) is composed of a very fine grained, turbid aggregate showing low birefringence; it contains a montmorillonite mineral (confirmed by x-ray diffraction), and locally has structure suggestive of the former presence of melilite. The turbid groundmass locally grades into pectolite.

Pectolite, which approximates 25 per cent of the rock, is the major component of the groundmass. It occurs as sheaflike and radial aggregates of fibers and blades that locally penetrate into the phlogopite

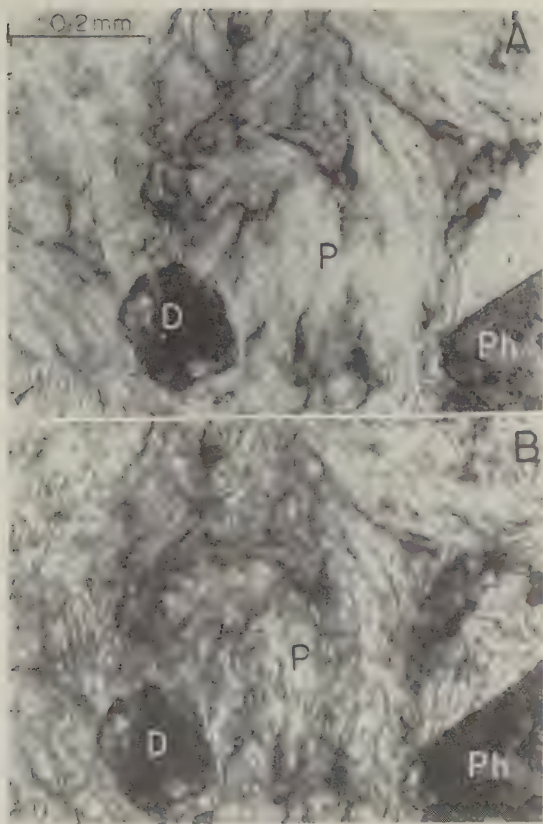


FIG. 1. Photomicrographs of pectolite-bearing rock, section 32, T. 26 S., R. 15 E., Woodson County, Kansas. A, plane-polarized light; B, crossed nicols. D, dolomite (?) clouded by leucoxene; P, pectolite; Ph, phlogopite.

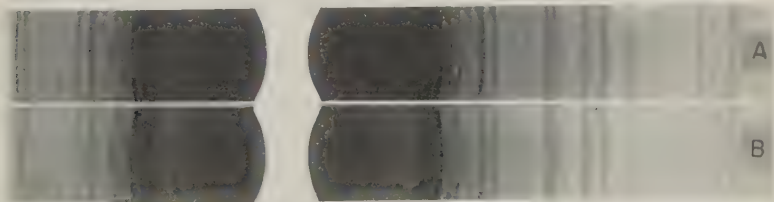


FIG. 2. X-ray powder films of pectolite. A, sample from section 32, T. 26 S., R. 15 E., Woodson County, Kansas; B, sample from Patterson, New Jersey.

books along cleavage traces and that grade into the turbid argillic part of the groundmass (Fig. 1). The blades and fibers range in length from nearly submicroscopic sizes to as much as 2 mm. Maximum width of the blades is about 0.1 mm. The blades and fibers have positive elongation, imperfect nearly parallel extinction, and strong birefringence (about 0.04), and are optically positive with moderate 2V. Locally they show cleavage that is both nearly parallel to and nearly normal to the length of the fibers. N_x is about 1.60, N_z about 1.64.

Comparison of x-ray powder films (Fig. 2) of pectolite from the peridotite with films of pectolite from Patterson, New Jersey, confirmed optical identification. d -values and intensities of the x-ray reflections (Table 1) for both the pectolite from the Hills Pond peridotite and the New Jersey sample proved identical.

Thanks are due Mr. Cecil T. Welch of Toronto, Kansas, who gave the writer permission to log drill core taken under Mr. Welch's supervision and to collect samples from the core.

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A PENETRATION-TWIN IN OLIVINE

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A porphyritic alkali basalt (A.U. thin-section 3560) from Khyber Pass, Auckland, contains numerous euhedra of olivine set in a finely felted groundmass of plagioclase, pyroxene, magnetite and glass. The olivine phenocrysts range in size up to 0.9 by 0.5 mm. and vary in composition from Fe_{81} to Fe_{90} . Their habit is fairly constant, the commonest combination of forms being $\{010\} + \{110\} \pm \{120\}$, together with $\{101\} + \{021\}$. True twinning was observed only in the one grain herein described, but the thin-section also contains euhedral olivine with "translation lamellae" oriented parallel to (100).

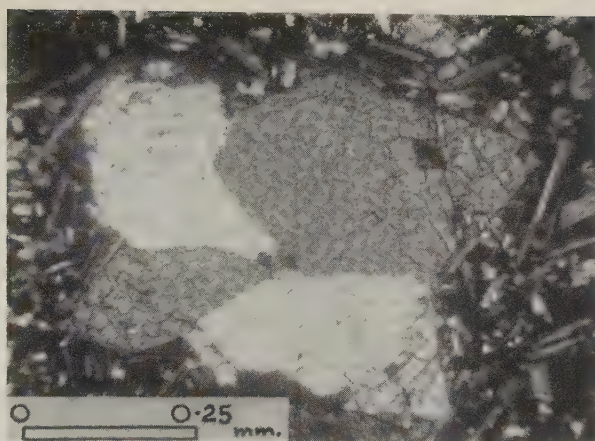


FIG. 1. Photomicrograph of olivine penetration-twin.

The penetration-twin has developed in a grain which, under crossed nicols, clearly consists of two idiomorphic individuals of approximately equal size (Figs. 1 and 2). The plane of the thin-section is almost normal to the Z vibration direction ($=a$) common to both individuals, so that the faces shown in Figs. 1 and 2 lie in the common zone $[100]$. Measurements around this zone reveal a slight difference in habit, for individual 1 displays the forms $\{010\} + \{021\}$ whereas individual 2 contains $\{010\} + \{021\} +$ one face of $\{001\}$. In both individuals there is an imperfect (010) cleavage and a distinct (001) parting.

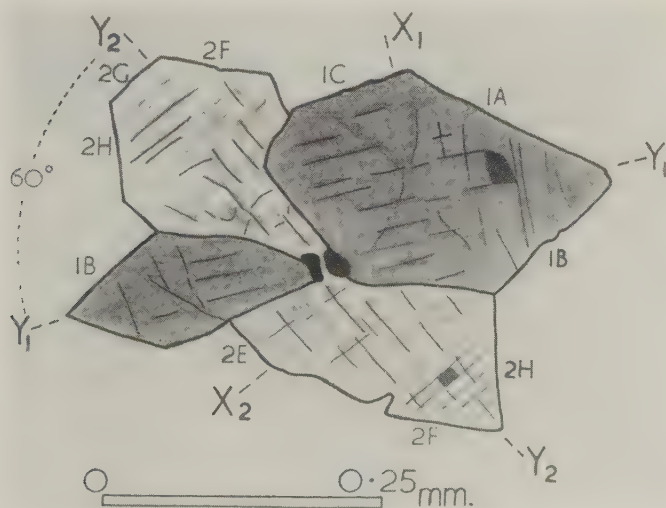


FIG. 2. Camera lucida drawing from Fig. 1, with face labels and optical directions.
 1A—(021), 1B—(021), 1C—(010), 2E—(010), 2F—(021), 2G—(001), 2H—(021).

A stereographic lower hemisphere plot of the optical directions within the penetration-twin is given in Fig. 3. The two sub-individuals 1 and 2 in the twin share a common $Z (=a)$ vibration direction, with the result that on the plot $Z_1=Z_2$ while X_1Y_1 and X_2Y_2 lie on the great circle normal to Z_{1-2} . The degree of rotation of X_1 from X_2 and of Y_1 from Y_2 was measured as 60° , with an estimated manipulative error of $\pm 1^\circ$. Face poles have also been inserted on Fig. 3. On the universal stage there is potentially a serious tilt error involved in the location of such face normals, but nevertheless the pole plots are quite close to the angular dispositions listed by Dana (1949, p. 597) for rational faces in this zone.

The stereographic plot shows that the twinning axis (labelled TA) must lie in the common zone $[100]$ and make an angle of $30^\circ \pm 1^\circ$ with both $Y_1 (=c_1)$ and $Y_2 (=c_2)$. Assuming an axial ratio close to $a:b:c=0.46:1:0.59$ of forsteritic olivine and utilizing Dana's (1949, p. 597) interfacial angles, the pole of the twin axis coincides on the stereogram with the theoretical position of the face pole for (011) . The law is thus twin axis $= \perp(011)$ or twinning plane $= (011)$. A similar twin for olivine has been reported in Dana's System (1909, p. 452).

The limitation of rotation, in this case 60° , in the zone $[100]$ is imposed by the structure parallel to (100) . Projection of the structure of olivine

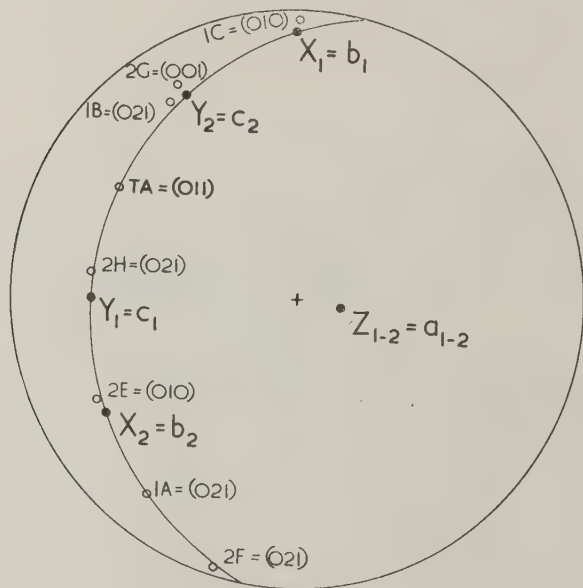


FIG. 3. Lower hemisphere projection of optical directions and face poles for the penetration-twin.

shows that a pseudohexagonal symmetry exists *within the tetrahedra* in the plane of (100), the atomic structure being similar in the trace directions of (001), (031) and (0 $\bar{3}$ 1). Alternative structures can therefore be built upon these planes which lie at an angle of 60° to each other.

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COMPROMISE GROWTH SURFACES ON PEGMATITE MINERALS

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Many crystals of pegmatite minerals display growth surfaces that form polygonal, step-sided pyramids. These are the "roots" of the crystals; the other parts display normal development, commonly with euhedral terminations. A search of available geological literature has failed to reveal a satisfactory explanation of this phenomenon.

The explanation offered here is that these anomalous pyramidal surfaces are the result of simultaneous growth of two adjacent crystals with different growth velocities. This process was described by Johnsen (1923) and is reviewed in Buckley (1951, p. 125-128).

Consider that crystal *A*, with growth velocities V and V' , has reached the stage shown in Fig. 1*a*, and crystal *B*, with growth velocities v and v' first begins to develop at point x . At some time later the two crystals have reached the stage shown by the solid lines in Fig. 1*b*, in which crystallization of crystal *A* has continued after crystal *B* has ceased to grow. The angles that the sides of crystal *B* make with the growth directions are ϕ and ϕ' , and simultaneous growth has taken place over the common distance S .

The resultant surfaces on crystal *B* are not in any rational way related to the axial systems of either crystal. They are called *compromise* surfaces and are the result of compromises between the relative growth velocities of the two substances.

If, for some reason, growth of crystal *A* ceased before crystal *B* ceased growing, crystal *B* could then terminate euhedrally outside crystal *A* (Fig. 1*c*). This is the situation occasionally encountered in pegmatites. In such examples the angle ϕ' cannot be measured. The only example in which ϕ' can be measured is that in which crystal *B* stops growing, even if only for a brief period, while growth of crystal *A* continues.

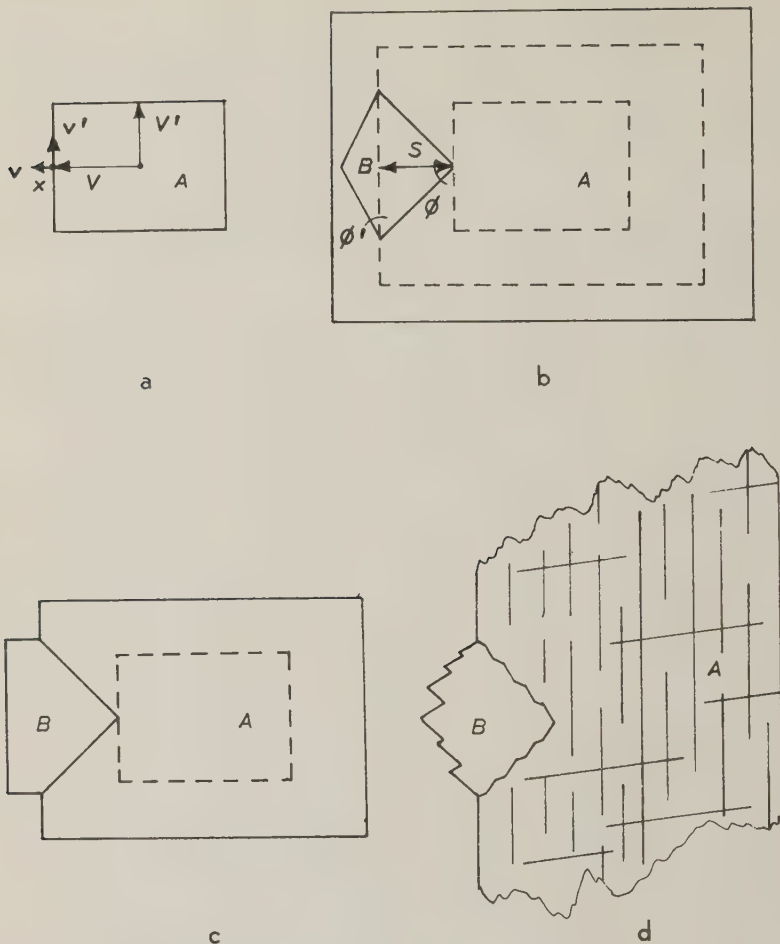


FIG. 1. Idealized representation of simultaneous growth stages.

The relationships illustrated are for the ideal situation in which the directions of growth in both crystallizing substances are tautozonal. The situation is far more complex when growth directions are askew, which is most commonly the situation. It should be mentioned here that adjacent materials of the same mineral can develop compromise faces if their growth directions are inclined to each other. This could account for the so-called "feather structure" observed on some columbites.

From the foregoing it is apparent that the anomalous pyramidal forms observed on some pegmatite minerals are compromise surfaces. The steps observed on many of these forms have yet to be explained.

Buckley (1951, p. 127) points out that the growth velocities of crystallization are dependent upon the temperature and concentration of the mother liquid. In the foregoing illustrations the constancy of the growth velocities was assumed and implies that the temperature and concentration remained constant. If either or both were to fluctuate, there would be a corresponding change in the growth velocities V , V' , v , and v' . The resulting changes in ϕ and ϕ' on the compromise surfaces would appear as steps if abrupt changes took place (Fig. 1*d*) and as curved surfaces if gradual changes took place. Both types are observed on some pegmatite minerals. It is suggested that the presence of steps on compromise faces is evidence that fluctuating conditions of temperature, and possibly concentration, existed in the immediate vicinity of the minerals displaying these features. It is further suggested that these fluctuations are the result of thermal convection within the pegmatite chamber during crystallization. Thus a crystal growing on the wall of the chamber would be subjected to fluctuating temperatures as the pegmatitic fluids circulated about the chamber. If the concentration of the fluids varied, then the crystal would grow more rapidly as the more concentrated portions passed by. For illustrative purposes the more concentrated portions might be termed concentration clouds. These hypotheses are illustrated in Fig. 2. The number of narrow planes forming steps on the compromise surfaces indicates the number of changes that have taken place during the period of simultaneous growth. The mean angles of the compromise planes forming the steps are represented by the general overall angles of the sides of the stepped pyramid (Fig. 1*d*).

These compromise growth shapes have been observed on several pegmatite minerals including cyrtolite, thorite, fluorite, gadolinite, monazite, multiple oxides, and quartz in simultaneous growth with microcline, mica, and clevelandite.

Cyrtolite

In Colorado numerous pegmatites contain cyrtolite displaying compromise growth surfaces. The South Platte area in particular has produced many excellent specimens. In these pegmatites crystal aggregates of cyrtolite 10 pounds or more in weight occur partially embedded in very large crystals of biotite that measure as much as 3 feet on an edge. The cyrtolite aggregates have euhedral terminations outside the biotite. These terminations display the curved tetragonal pyramids so typical of cyrtolite. Within the biotite, however, the cyrtolite "roots" are finely stepped polygonal compound pyramids. Generally the cyrtolite c axes are oriented approximately normal to the basal cleavage of the biotite. An approximation of the average ϕ is 60° , indicating that cyrtolite grew

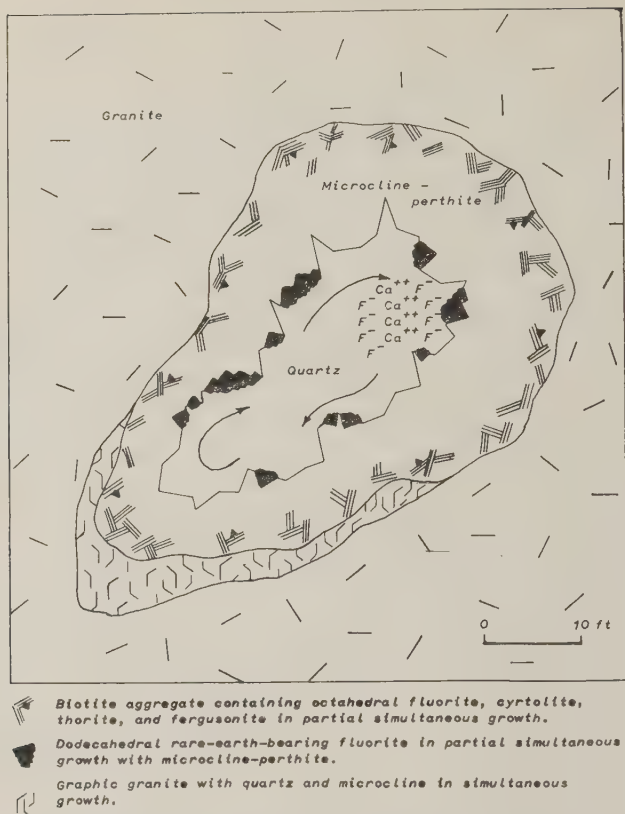


FIG. 2. Diagrammatic cross section of a South Platte area, Colorado, pegmatite showing hypothetical thermal convection currents and concentration cloud.

laterally at a greater rate than biotite grew vertically with respect to its basal cleavage plane. The fine steps, some of which are superimposed upon larger steps, indicate that temperature, and possibly concentration, fluctuated relatively rapidly though irregularly. Many of the steps are less than 0.1 mm. high. In general outline the basal cross section of the pyramidal "roots" is irregular or somewhat rounded due, in part, to individual crystals in the aggregate being askew with respect to each other.

Thorite

In addition to cyrtolite, there is also thorite in some of the South Platte pegmatites. It is less abundant than cyrtolite with which it usually occurs in subparallel growth. In some examples the boundary surface between cyrtolite and thorite displays compromise stepped

growth surfaces. The thorite crystals commonly have their "roots" in biotite as does cyrtolite; however, the average angle ϕ is somewhat smaller than that of cyrtolite. This indicates that the lateral growth velocity of cyrtolite exceeded that of thorite and that both of these exceeded the vertical velocity of biotite with respect to the biotite cleavage plane.

Fluorite

The White Cloud pegmatite near South Platte, Colorado contains rare-earth-bearing fluorite which occurs in several zones. In the outer intermediate zone octahedral fluorite occurs with "roots" showing stepped compromise surfaces in biotite. The "roots" on individual fluorite octahedra are flat, stepped, four-sided pyramids. The average ϕ of the fluorite is approximately 80° . Cyrtolite, associated with the fluorite has a smaller ϕ and fergusonite, associated with cyrtolite has ϕ less than that of cyrtolite. Thus the lateral growth velocity of fluorite exceeds that of cyrtolite, which, in turn, exceeds that of fergusonite.

Fluorite with stepped surfaces occurs in the inner intermediate zone with "roots" in perthitic microcline and euhedral terminations in quartz of the core. These fluorite crystal aggregates display distorted dodecahedral forms and the "roots" are stepped pyramids with six or more sides. Some masses weigh upwards of 10 pounds. In one area of approximately 1 square yard (Fig. 3) there are at least 17 "roots" exposed in quartz by the removal of feldspar. Individual steps can be correlated from crystal to crystal. Corresponding steps have the same height irrespective of the size of the crystal. These relationships are to be expected if the steps are caused by convection. They help support the hypotheses proposed in this paper. At a particular time during crystallization all of the fluorite crystals in a localized area are subjected to the same conditions of temperature and concentration, so compromise surfaces are all developing simultaneously at the same rate and with the same angle ϕ . When, because of thermal convection, the temperature, and possibly the concentration, changes, the growth velocities change simultaneously on all fluorite crystals within the localized environment. Thus during any given period nearly identical steps are formed on compromise surfaces of crystals within the same local environment of temperature and concentration. This process is represented diagrammatically in Fig. 2.

In a pegmatite $1\frac{1}{2}$ miles northeast of Foxton, Colorado, some fluorite crystals have been completely included by microcline during simultaneous growth. Some of these fluorite crystals are doubly terminated with six-sided pyramids displaying stepped surfaces (Fig. 4).



FIG. 3. (Left) Mining of feldspar at the White Cloud mine has exposed several "roots" of rare-earth bearing fluorite that grew simultaneously with microcline-perthite, and that terminates dodecahedrally in quartz. The mass of microcline-perthite to the left of the Brunton compass has been removed from the fluorite "root" above and slightly to the right.

FIG. 4. (Right) Detailed view of stepped compromise surfaces on rare-earth bearing fluorite from the South Platte area, Colorado. Maximum dimension is about 5 cm.

Gadolinite

Compromise surfaces have been observed on gadolinite from Benton's prospect near Cotopaxi, Colorado. Some of these crystals occur in primary microcline, which indicates that gadolinite also is a product of primary crystallization, having grown simultaneously with microcline. Thus, some gadolinites are not necessarily a product of a replacement stage of crystallization. At Roscoe Dike, on Clear Creek west of Golden, Colorado, some gadolinite crystals are included in albite. It is suggested that the albite selectively replaced primary microcline and left the gadolinite unaffected, except perhaps for superficial alteration.

Some gadolinite crystals with compromise surfaces in contact with biotite occur at Roscoe Dike and in the South Platte area. The stepped pyramids on these gadolinites are extremely flat with ϕ near 90° . This indicates that biotite crystallization had practically ceased when the gadolinite started to crystallize.

Monazite and Xenotime

An aggregate of two monazite crystals from the Bucky mine, Quartz Creek district, Colorado (Staatz and Trites, 1955, p. 61) occurs in simultaneous growth with clevelandite. The compromise surfaces are not stepped which indicates crystallization under constant conditions of concentration and temperature. Stepped compromise surfaces have been noted on xenotime from Benton's prospect near Cotopaxi, Colorado.

Multiple Oxides

Compromise surfaces have been observed on samarskite, fergusonite, betafite, and several unidentified multiple oxides. Most of these forms have been the result of simultaneous growth with biotite. Most of the betafites from Madagascar illustrated by Lacroix (1922) display compromise surfaces on "roots" in biotite.

Quartz

Compromise surfaces between quartz and microcline are common features in many pegmatites, and the cuneiform-like intergrowths in graphic granite display compromise surfaces, some of which are minutely stepped. Such examples are given as evidence in support of simultaneous growth of microcline and quartz in some graphic granite.

CONCLUSION

The recognition of compromise growth surfaces between two minerals is evidence for simultaneous growth. Only in ideal examples can the growth velocities be determined by the relationships stated by Johnsen (1923). Some examples, however, are suitable for an approximation of relative velocities in two directions normal to each other.

It is suggested that steps on compromise surfaces may be evidence for thermal convection within the system, whereby two mineral phases in simultaneous growth are subjected to cyclic changes in temperature and possibly concentration. Those changes alter the relative growth velocities periodically, produce successive planes with different values of ϕ and ϕ' and thus give rise to steps.

Correct interpretation of compromise surfaces aids in determining the paragenetic sequence in pegmatites.

ACKNOWLEDGMENTS

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UNUSUAL GALENA FROM THE BOULDER BATHOLITH, MONTANA¹

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During studies of some uranium-bearing veins in the Boulder batholith, Montana, a mineral of unusual appearance was encountered in polished sections of ore from the Lone Eagle mine. This mineral was ultimately proven to be galena, and it was called galena "B" (Wright and Shulhof, 1957) to distinguish it from the associated ordinary galena "A." In polished section the unusual galena resembled uraninite, so much so that it proved impossible to identify the two by simple observation. Because of the importance of uraninite in these studies the impostor had to be carefully worked out. Further, a comparison of the isotopic composition of a possibly radiogenic galena with that of associated common galena could have important bearing on the interpretation of age and origin of the "siliceous reef" and the "base metal" uraniferous deposits of the batholith (Wright, 1956).

Galena "B" is in formless, somewhat rounded blebs ranging from a few microns to 0.5 mm. in length. In polished sections it appears as a soft (hardness B), seemingly sectile, opaque mineral having a tan to gray color and low but variable reflectivity resulting in a faintly mottled appearance. Some of the galena "B" is intergrown with other ore minerals, especially uraninite, although most is in isolated blebs in the microcrystalline quartz gangue. Etch tests with the usual reagents suggested galena, and microchemical tests confirmed lead and silver. The lack of the characteristic cleavage pits, high polish and white color of galena masked its identity for some time.

¹ Contribution No. 58-119 from the College of Mineral Industries, The Pennsylvania State University, University Park, Pa.

A qualitative spectrographic analysis of carefully selected material indicated the following approximate composition for the unidentified mineral:

Pb	10%	Mg	<0.1%
Ag	0.1-10%	Fe	<0.1%
Mo	0.1-10%	Ca	<0.1%
Si	0.1-10%	Cu	<0.1%
Al	<0.1%	V	Not detected
Sb	<0.1%	Th	Not detected

A qualitative wet-chemical analysis showed roughly 10% of sulfur. Selenium was not detected.

Alpha autoradiographs of several polished sections showed no appreciable activity in blebs of microscopically pure galena "B." They did prove useful for differentiating the mineral from uraninite by direct comparison of the polished section and autoradiograph using a comparison eyepiece.

Powder x-ray diffraction photographs confirmed galena conclusively, with quartz the only determinable impurity.

Fine crystal size seemed a possible explanation for the unusual appearance and properties of galena "B." Randomly oriented crystallites of a few microns' diameter should result in a lower polish and variable reflectivity, and a gray rather than white color in vertical illumination. This would also account for the lack of characteristic cleavage pits. A Laue x-ray photograph showed concentric circles, some continuous, others of closely spaced spots. The pattern confirmed the fine crystal size of the galena and suggested an approximate diameter for individual crystallites on the order of 10^{-4} cm. (Taylor, 1952).

The presence of uranium as a source of lead was considered in connection with the association of very sparsely distributed, minutely crystalline galena, with rather abundant ordinary galena. J. Laurence Kulp and Donald S. Miller of the Lamont Geological Observatory, Columbia University, provided lead isotope analyses of the two galena varieties. The isotopic analysis of the ordinary galena "A" is as follows:

Pb ²⁰⁴	Pb ²⁰⁶	Pb ²⁰⁷	Pb ²⁰⁸
1.362 ± 0.008	24.77 ± 0.07	21.28 ± 0.06	52.60 ± 0.08

Galena from six other mines in the Boulder batholith has a similar isotopic composition. No significant difference was reported* in the analysis of galena "B," and the presence of uranium as a source of lead appears to have had little to do with its composition.

Two other explanations of galena "B" were considered: (1) colloidal

* Dr. Donald S. Miller, oral communication.

deposition and (2) grain for grain replacement of the uraninite. The possibility of colloidal deposition receives a little support from the close association of galena "B" with microcrystalline quartz gangue containing small grains of cryptocrystalline uraninite and microscopic grains of pyrite, sphalerite and some other sulfides (Wright and Shulhof, 1957). This association represents a second stage of mineralization in the Lone Eagle Mine, apparently contemporaneous with the introduction of the "siliceous reef" uraniferous veins having an essentially identical assemblage. The ordinary galena "A," on the other hand, occurs with megacrystalline quartz and base metal sulfides of an apparently earlier mineralization stage related to the large base metal deposits of the batholith (Wright, 1956).

Objections to the colloidal idea are the lack of any textural evidence (botryoidal outlines, syneresis cracks, etc.) in the galena itself, or in the associated minerals (except uraninite).

Grain-for-grain replacement of uraninite by galena appears to agree most nearly with the observed facts. The formless rounded blebs of galena resemble the associated uraninite both in shape and in their generally isolated occurrence in microcrystalline quartz. The crystallite diameter of the galena "B" lies within the range ($<10^{-3}$ cm.) observed for pitchblende (Croft, 1954). More direct evidence is found in the intimate association of uraninite with galena "B" in a few grains.

It appears that the intriguing thought of radiogenic galena of unusual habit occurring with galena of normal habit and isotopic composition, must be discarded in favor of a more commonplace process, replacement.

This study was conducted in the laboratories of the Mineral Industries College, The Pennsylvania State University, in connection with Contract AT(30-1)-1390 with the U. S. Atomic Energy Commission.

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OCCURRENCE OF WAIRAKITE IN METAMORPHIC ROCKS
OF THE PACIFIC NORTHWEST*

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During a preliminary study of low grade metamorphic tuffs and tuff breccias, wairakite ($\text{CaAl}_2\text{Si}_4\text{O}_{12} \cdot 2\text{H}_2\text{O}$), the calcium analogue of analcite, was found in a number of specimens from the Keechelus (?) formation in the Mr. Rainier National Park, Washington. This is believed to be the first reported occurrence of wairakite in metamorphic rocks. Steiner (1955) first described the occurrence and optical and physical properties of wairakite from (the active hydrothermal area of) Wairakei, New Zealand. Coombs (1955) presented x-ray data.

Wairakite, as well as several other very fine grained zeolites, occurs in the low grade metamorphic tuffs of the Keechelus (?) formation. Identifications are based primarily on x-ray diffraction patterns. About 2 gms. of a rock are crushed to pass 120 mesh, and then centrifuged in bromoform diluted with acetone to a density of about 2.40 gms./ml. All zeolites float and a yield of 0.1 gms. is not uncommon. Minor impurities in the separations are quartz and chlorite.

To safely distinguish wairakite from analcite, the (400) peak ($2\theta_{\text{CuK}\alpha} = \text{approx. } 26.2^\circ$) must be scanned at a speed of $\frac{1}{4}^\circ/\text{min}$. This reflection, as well as others, will show double peaks (Coombs, 1955). Table I presents d -spacings of a Keechelus wairakite and the New Zealand wairakite. In six observed wairakites from different localities the d -spacing of the peaks referred to as (400) show only slight variations.

In the tuffs wairakite occurs in cavity fillings, in replaced plagioclase crystals, and in the groundmass. Figures 1 (plane light) and 2 (crossed nicols) illustrate the replacement of a plagioclase crystal by a fine meshwork of wairakite. The grain size of individual wairakite crystals is very small (commonly less than 0.02 mm.). Typical of coarser material is a crossed lamellar twinning (see Steiner, 1955, p. 692, Fig. 2). Similar twinning was found frequently in the wairakite from Mt. Rainier. For example, most of the wairakite in Fig. 2, if viewed under high power, will show such twinning.

Due to the very fine grained nature, most physical and optical properties could not be determined. Refractive indices were found to be:

$$\begin{aligned}\alpha &= 1.500 \quad \pm 0.001 \\ \gamma &= 1.501 \quad \pm 0.001 \\ \gamma - \alpha &= 0.001 \text{ to } 0.0005\end{aligned}$$

* This work was supported in part by a grant from the National Science Foundation.

TABLE I. X-RAY DATA FOR WAIRAKITE FROM THE KEECHELUS FORMATION, COMPARED TO THAT FROM NEW ZEALAND (COOMBS, 1955). $\text{CuK}\alpha$ RADIATION WITH A SCANNING SPEED OF $\frac{1}{2}^\circ/\text{MINUTE}$

Keechelus wairakite		New Zealand wairakite	
$d \text{ \AA}$	I	$d \text{ \AA}$	I
6.850	35	6.85	4
5.577	77	5.57	8
4.840	35	4.84	4
3.654	23	3.64	3
3.412*	100	3.42	8
3.390*	92	3.39	10
3.21	14B	3.21	1B
3.05	6B	3.04-3.06	1B
2.918*	52	2.909	5
2.900*	37	2.897	3
2.79	5	2.783	1
2.770	6	2.770	1
2.681	17	2.680	4
2.675	9	2.67	1
2.506	11	2.50	1
2.491	15	2.489	4
2.416	10	2.418	3
		2.35	1B
		2.26-2.28	1B
2.214	9	2.215	4
		2.17	1
		2.147	1
		2.115	1
		2.095	1
1.996	2	1.996	2
		1.93	1B
1.89	9B	1.886-1.895	3B
		1.867	1
1.857	8	1.857	3
		1.844	1
		1.822	1B
1.701	14	1.722-1.732	4B
		(continues)	

*—determined from scanning speed of $\frac{1}{4}^\circ/\text{min.}$ with quartz as an internal standard.

I—arbitrary intensity scale.

B—broad peak (or line).

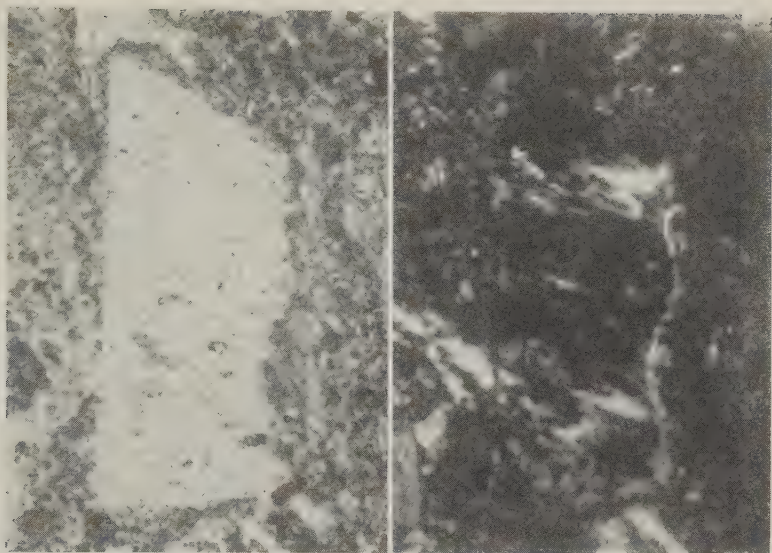


FIG. 1. (Left) Wairakite (with some small grains of epidote and chlorite) replacing a plagioclase crystal in a tuff breccia consisting of rock fragments and a fine-grained groundmass. The groundmass is composed mostly of chlorite, wairakite, unaltered plagioclase, leucoxene, and celadonite. Plane light, $\times 130$.

FIG. 2. (Right) Same as Fig. 1 under crossed nicols. The wairakite is nearly black, while the unaltered plagioclase remains light. $\times 130$.

Wairakite in the groundmass of an average tuff looks very similar to glass or analcite, except for a faint birefringence, occasional crossed twinning, and a lack of cleavage planes.

I am indebted to Dr. Hans P. Eugster for helpful criticism and discussions.

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NEW MINERAL NAMES

1 Tc—Strontiohilgardite, 2 M (Cc)—Calciumhilgardite (= Hilgardite), 3 Tc—Calciumhilgardite (= Parahilgardite)

OTTO BRAITSCHE. 1 Tc—Strontiohilgardit, $(\text{Ca}, \text{Sr})_2 [\text{B}_5\text{O}_8(\text{OH})_2\text{Cl}]$ und seine Stellung in der Hilgarditgruppe, $\text{X}_2 [\text{B}_5\text{O}_8(\text{OH})_2\text{Cl}]$. *Beiträge Mineral. u. Petrog.*, **6**, 233–247 (1959).

Strontiohilgardite was found in insoluble residues from "Hartsalz" of the 820 m. level of the Königshall-Hindenburg IIK mine, Meyershausen, Germany. The sample contained about 37 vol. % sylvite, 37% halite, 22% dense white anhydrite. Other insoluble minerals were anhydrite, quartz, mica, clays, celestite, K feldspar, magnesite, hematite, and Fe-boracite.

The mineral occurs as crystals with max. dimensions 2 mm. long, 1 mm. wide, 0.5 mm. thick. Crystal forms observed (010), (0 $\bar{1}$ 0), (dominant), (100), (1 $\bar{0}$ 0), (001), (00 $\bar{1}$), (101), (011), (120), and (111). Measurements of 13 crystals (5 left, 8 right) were made. Triclinic, pedial, $a:b:c = 0.9845:1:1.0198$, α 75.4°, β 61.2°, γ 60.5°. Twinning not observed. Piezoelectric. Precession, rotation, and Weissenberg photographs gave a_0 6.38, b_0 6.489, c_0 6.608 Å, space group P 1, $Z=1$. Cleavage (001 good, (211) distinct. Indexed x -ray powder data are given. The strongest lines are 2.89 (s), 2.82 (s), 2.775 (s), 2.142–2.137 (ms), 2.092 (ms), 1.986 (ms), 1.829 (ms, broad).

The mineral is colorless to pale yellow, luster vitreous to adamantine. Hardness 5–7. G . 2.99₃ (suspension method). Optically biaxial, positive, n_s (at 500 μ), α 1.638, β 1.639 (calcd.), γ 1.670, $2V$ $19 \pm 3^\circ$, optic axis nearly parallel to [100], $\gamma':[\bar{1}00] = 21 \pm 1^\circ$. For α , $\phi - 146^\circ$, ρ 14°; for β , $\phi - 6^\circ$, ρ 79°; for γ , ϕ 86°, ρ 81°.

Spectrographic analysis on 6 mg. by Braitsch with x -ray fluorescence determination of Sr and microchemical determinations by O. Pfundt of Cl and H₂O gave B₂O₃ 40–45, CaO 15–20, SrO 20–25, Cl 8.2, H₂O 5.3, Al₂O₃ 0.2, MgO 0.1, SO₃ n.d., sum 90–105%. Calculation of the molecular weight from the unit cell and G . indicate Ca: Sr = 1.08:0.92. The formula $\text{Ca}_{1.08}\text{Sr}_{0.92} [\text{B}_5\text{O}_8(\text{OH})_2\text{Cl}]$ requires B₂O₃ 46.37, CaO 26.13, SrO 25.39, Cl 9.44, H₂O 4.80%.

Partial analyses showed SrO 1.3% in hilgardite and 1.6% in parahilgardite from the type localities. If the original analyses (see Dana's System, 7th Ed., Vol. II, pp. 382–382) are corrected for the SrO present, the formulas of both are closer to $\text{Ca}_2\text{B}_5\text{O}_8(\text{OH})_2\text{Cl}$ than to the formula previously given, $\text{Ca}_8\text{B}_{18}\text{O}_{33}\text{Cl}_4 \cdot 4\text{H}_2\text{O}$.

Restudy of hilgardite and parahilgardite showed previous x -ray data to be partly in error. The new data are:

	Strontiohilgardite Reyershausen	Hilgardite Choctaw	Parahilgardite Choctaw
Symmetry	Triclinic	Monoclinic	Triclinic
Space group	P 1	C c	P 1
a_0 (Å.)	6.38	6.31	6.31
b_0 (Å.)	6.480	11.33	6.484
c_0 (Å.)	6.608	11.44	17.50
α	75.4°	90°	84.0°
β	61.2°	90°	79.6°
γ	60.5°	90°	60.9°
Cell vol. (Å ³)	208	817	615
Z	1	4	3

To show the relationships of the polymorphs, the names suggested are: 1 Tc—Strontiohilgardite, 2 M (Cc)—Calciumhilgardite (= Hilgardite), 3 Tc—Calciumhilgardite (= Parahilgardite).

DISCUSSION—The naming of polymorphs in a manner showing the type of structure (wurtzite—4H, muscovite—1M, etc.) has many advantages and is coming into wide use. But using the terms as prefixes is confusing. Why not instead hilgardite—2M for hilgardite, hilgardite—3Tc for parahilgardite, and strontian hilgardite—1 Tc for strontiohilgardite?

MICHAEL FLEISCHER

Hellyerite

K. T. WILLIAMS. Nickel mineralization in western Tasmania. *Australasian Inst. Mining and Metallurgy*, **F. L. Stillwell Anniversary Vol.** (December 1958), pp. 263–302.

The name hellyerite is given to a light blue mineral of composition $\text{NiCO}_3 \cdot 6\text{H}_2\text{O}$ found as a secondary coating on nickel ore at the Lord Brassey Mine, Heazlewood. A full description was published in the *Am. Mineral.*, **44**, 533–538, 1959.

M. F.

Unnamed ($2\text{Na}_2\text{SO}_4 \cdot \text{CaSO}_4 \cdot 2\text{H}_2\text{O}$?)

FRED BENINGTON. Preliminary identification of crystalline phases in a transparent stalactite. *Science*, **129**, 1227 (1959).

Glassy stalactites found in the Flint Ridge Cavern system of south-central Kentucky effloresced and melted when brought above ground. Samples transported to the laboratory under a cool, water-saturated atmosphere, consisted of two phases. The major phase melted at $33\text{--}34^\circ\text{C}$., had “the refractive index 1.40 and sp. gr. 1.46,” and is therefore identified as mirabilite. Solution of the mirabilite in an ice cold alcohol-water mixture gave about 1 per cent of insoluble material, occurring in monoclinic needles. It was slightly soluble in water, readily soluble in dilute HCl. The solution contained Na, Ca, and SO_4 with spectroscopic traces of Mg, Al, and Si. Analysis gave $\text{Na}:\text{Ca}=3.821$. The loss in weight at 125° in a vacuum was 7.9–8.0 per cent. It is suggested that this is the compound $2\text{Na}_2\text{SO}_4 \cdot \text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ synthesized by Hill and Wills, *J. Am. Chem. Soc.*, **60**, 1647 (1938), by the action of Na_2SO_4 solution on gypsum, and which is not a stable phase at 25° or above. “The measured refractive index is 1.518”; Hill and Wills reported 1.510.

DISCUSSION.—Adequate optical and x-ray data must be provided before this can be accepted.

M. F.

NEW DATA

Ianthinite

C. GUILLEMIN AND J. PROTAS. Ianthinite et wyartite, *Bull. soc. franç. mineral. crist.*, **82**, 80–86 (1959).

Re-examination of 6 samples of ianthinite from 3 localities shows it to be orthorhombic with $a_0\ 11.52 \pm 0.05$, $b_0\ 7.15 \pm 0.02$, $c_0\ 30.3 \pm 0.1\ \text{\AA}$, $a:b:c=1.611:1:4.238$, $Z=4$. Cleavage (001) perfect, also (100). Color black to violet, streak brownish-violet. Hardness 2–3. $G\ 5.16 \pm 0.05$. Optically biaxial, neg., n_s , $\alpha\ 1.685 \pm 0.002$, $\beta\ 1.91 \pm 0.01$, $\gamma\ 1.93 \pm 0.01$. Strongly pleochroic, X (=c) colorless, Y (=b) purple, Z (=a) violet. The formula of Big-nand (1955) was $\text{UO}_{2.84} \cdot x\text{H}_2\text{O}$. A new determination of H_2O gave 9.90%, which gives

$\text{UO}_2 \cdot 34 \cdot 1.76\text{H}_2\text{O}$ or $\text{UO}_2 \cdot 5\text{UO}_3 \cdot 10.56\text{H}_2\text{O}$. A D.T.A. curve shows a large endothermic break at about 100° , a small exothermic break at 320° (oxidation of $\text{UO}_2?$), and an endothermic break at 630° . X-ray powder data are given.

M. F.

DISCREDITED MINERALS

Epi-ianthinite (= Schoepite)

C. GUILLEMIN AND J. PROTAS. Ianthinite and wyartite, *Bull. soc. franç. mineral. crist.*, **82**, 80–86 (1959).

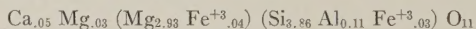
Epi-ianthinite (Schoep and Stradiot, *Am. Mineral.*, **32**, 344–350 (1947); Frondel, *U. S. Geol. Survey Bull.* **1054**, 60–62 (1958)) is probably schoepite. All samples of ianthinite examined showed yellow pseudomorphs that correspond to "epi-ianthinite" and give x-ray patterns practically identical with that of schoepite. It is not clear, however, whether the type material was re-examined.

M. F.

Aphrodite (= Stevensite)

C. CAILLÈRE AND S. HÉNIN. Une probleme de nomenclature: les montmorillonites magnésiennes (Saponite—aphrodite—rassoulite—stevensite). *Bull. groupe franç. argiles* **8**, No. 3, 37–40 (1956).

Restudy of aphrodite (Berlin, 1840, Dana's System, 6th Ed., p. 675) shows it to be a member of the montmorillonite group with formula (water-free basis) of



It is suggested that the single name saponite be used for saponite, aphrodite, rassoulite (ghassoulite), and stevensite, or that saponite be used for material showing appreciable tetrahedral substitution, stevensite for material showing only slightly tetrahedral substitution.

DISCUSSION.—The name aphrodite (1840) has priority over stevensite (1873), but since the name had not been used for over a hundred years, priority may be set aside. The second suggestions above is preferred; it is recommended that the names stevensite and saponite be retained.

M. F.

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